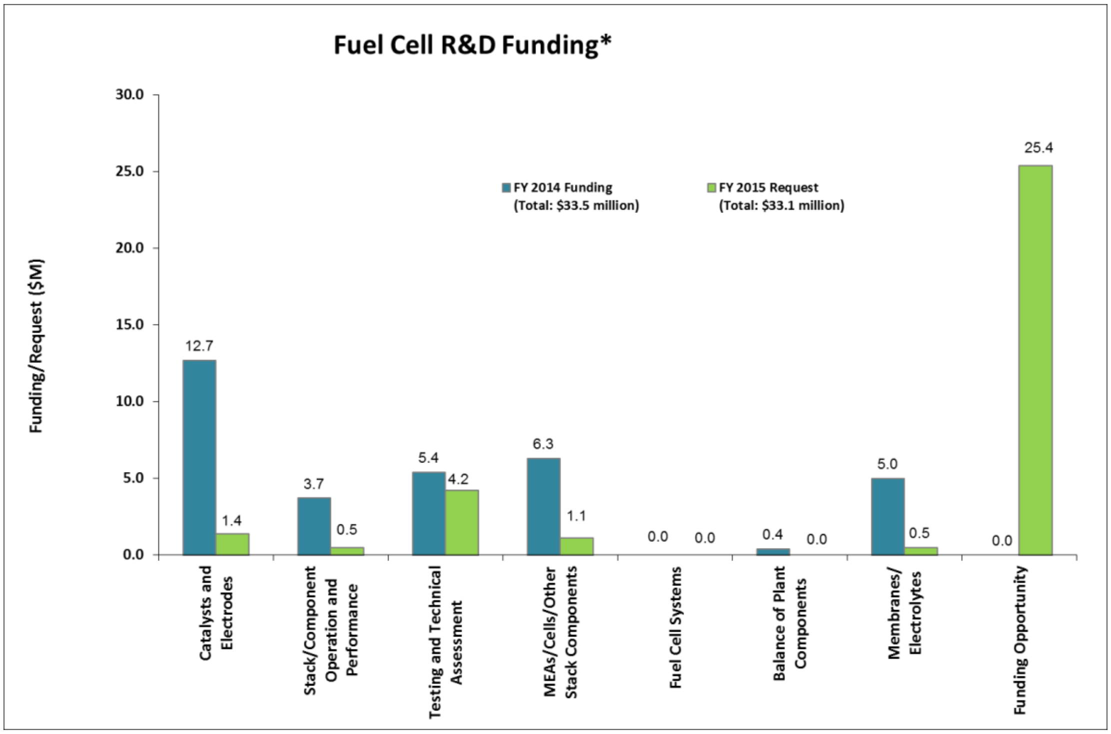
2014 — Fuel Cells
Summary of Annual Merit Review of the Fuel Cells Sub-Program

Summary of Reviewer Comments on the Fuel Cells Sub-Program:

Reviewers felt that there was a good balance between near-, mid-, and long-term research and development (R&D) in the Fuel Cells sub-program. Reviewers agreed that cost and durability are the major technical challenges and praised efforts taken by the Fuel Cells sub-program to address these issues. A strength of the sub-program, as noted by the reviewers, is its well-structured, focused, and well-managed projects. Reviewers also stated that the project teams are strong and feature excellent collaboration between academia, industry, and the national laboratories. Input from the community—for example, via the U.S. Council for Automotive Research—was also identified as a strength in focusing R&D on the most relevant challenges. Reviewers noted that many of the projects in the current portfolio are ending and expressed optimism that the next funding opportunity announcement will address current gaps in the portfolio. Specifically, reviewers identified understanding degradation mechanisms, developing new analytic tools and increasing access to existing tools, and accelerating integration of recently developed materials into cells and stacks as areas that need to be addressed. Some reviewers expressed a desire to see more effort to develop a domestic supply base for critical components and achieve better transfer of technology from the laboratories to industry.

Fuel Cells Funding:

The sub-program received $33.5 million in fiscal year (FY) 2014. The request for FY 2015 is $33.1 million. The focus of the sub-program is on reducing fuel cell costs and improving durability. Efforts include approaches that will achieve increased activity and utilization of platinum group metal (PGM) and PGM-alloy catalysts, as well as non-PGM catalysts for long-term applications; ion exchange membranes with enhanced performance and stability at reduced cost; improved integration of catalysts and membranes into membrane electrode assemblies (MEAs); and a better understanding of degradation mechanisms and mass transport. Two new projects were funded in FY 2013 and initiated in FY 2014, and one new project was funded in FY 2014 from the most recent solicitation.



* Subject to appropriations, project go/no-go decisions, and competitive selections. Exact amounts will be determined based on research and development progress in each area and the relative merit and applicability of projects competitively selected through planned funding opportunity announcements.

Majority of Reviewer Comments and Recommendations:

At this year's review, 42 projects funded by the Fuel Cells sub-program were presented, and 27 were reviewed. Projects were reviewed by between 7 and 12 reviewers, with a median of 10 experts reviewing each project. Reviewer scores for these projects ranged from 2.6 to 3.6, with an average score of 3.2. This year's highest score of 3.6 and average score of 3.2 were similar to last year's highest and average scores of 3.6 and 3.1, respectively. The lowest score of 2.6 for all projects reviewed in 2014 was a modest improvement over 2012's low score of 2.4.

Catalysts and Electrodes: The scores for the nine catalyst projects ranged from 2.6 to 3.6, with an average of 3.1. Reviewers praised the highest-rated project for making good progress toward meeting U.S. Department of Energy (DOE) targets, and for applying a solid understanding of surface science to catalyst development. For the lowest-scoring project, development of durable catalyst supports, reviewers felt that the results for the selected metal oxide supports do not yet meet the performance requirements for use in fuel cells, although the reviewers liked the approach.

Stacks and Component Operation and Performance: Four projects were reviewed, receiving scores between 2.9 and 3.4, with an average score of 3.2. Reviewers praised the highest-rated project's approach to studying durability for its strong combination of characterization, diagnostics, and modeling. Reviewers noted that, although the approach is thorough, its focus is limited and would benefit from an expanded material set and a deeper parametric study. Reviewers felt that the lowest-scoring project's approach was generally good and addressed the known durability issues in polymer electrolyte membrane (PEM) fuel cells; however, they expressed concern about an overlap with efforts being pursued by automotive and fuel cell stack original equipment manufacturers (OEMs) and a lack of automotive OEM collaboration.

Testing and Technical Assessment: Seven projects were reviewed and received scores between 3.1 and 3.6, with an average score of 3.3. According to reviewers, the analysis and testing projects take a good approach and produce highly relevant analyses for the fuel cell community. In some cases, reviewers questioned assumptions being made and recommended interaction with OEMs to refine assumptions where possible.

MEAs, Cells, and Other Stack Components: Three projects were reviewed in this area, receiving scores of 3.0, 3.1, and 3.2. Reviewers considered the projects to have well-coordinated teams that achieved good technical progress. Reviewers noted that current approaches should be aimed at addressing operational robustness in practical applications for thin-film catalysts.

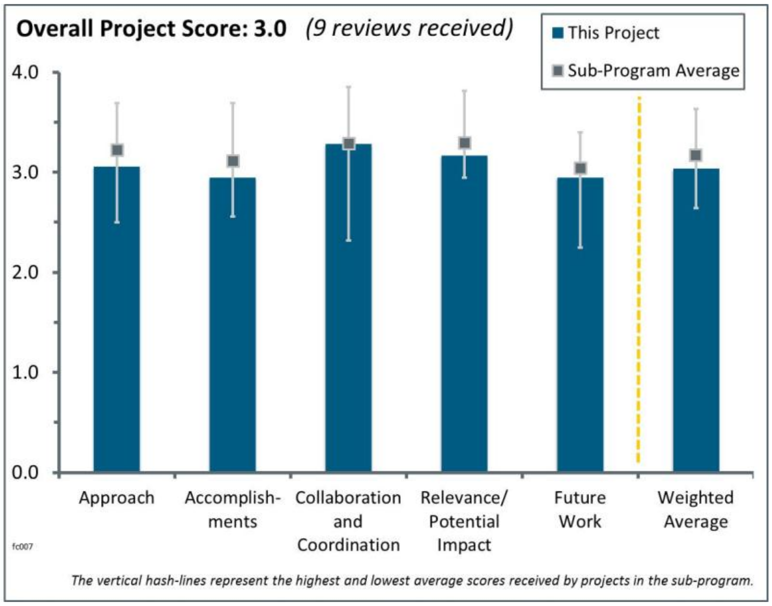
Fuel Cell Systems: The one project reviewed this year received a score of 3.3. According to reviewers, good technical progress has been made toward simplifying the system design and reducing part count and cost. Some reviewers expressed concern that there was not a business case for hydrogen from renewable biofuel. They also noted that durability still needs to be demonstrated.

Balance-of-Plant Components: One project, development of a compressor/expander unit, was reviewed. It received a score of 3.1. Reviewers regarded the focus of this project as very important for successfully launching fuel cell electric vehicles. While reviewers characterized the upstream (i.e., sub-system and system-level) partnerships as strong, they suggested that the project could benefit from a motor/controller partner, noting that these components seem to be the primary barriers to meeting the cost target. Reviewers lauded the project for its progress in modeling, improvement of designs, and hardware testing, but they saw overall progress as relatively slow.

Membranes/Electrolytes: The two membrane projects reviewed received scores of 2.9 and 3.2. Reviewers indicated that the highest-rated project has made good progress toward meeting DOE targets, using sound approaches to combine high conductivity, low swelling, and mechanical stability. Reviewers expressed concern about the scalability and manufacturing cost for both projects.

Project # FC-007: Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

Bryan Pivovar; National Renewable Energy Laboratory



Brief Summary of Project:

In the current review period, this project pursued synthesis of novel extended thin-film electrocatalyst structures (ETFECSs) and incorporated ETFECSs in membrane electrode assemblies (MEAs) to meet the U.S. Department of Energy (DOE) targets for fuel cell cost, performance, and durability. The approach includes developing durable, high mass activity, extended-surface Pt catalysts and optimizing MEA performance/durability for these materials.

Question 1: Approach to performing the work

This project was rated **3.1** for its approach.

- The project focuses on the key barriers of activity and durability. During the last year of the project, there has been much better balance between synthesis, characterization, and making electrode assemblies. The team has focused on the galvanically displaced samples and put more effort into MEA testing. The initially unique approach to incorporate extended thin films into thick electrode architectures has shifted to less controlled systems. The team has acknowledged that the initial goals were too difficult to achieve and that, if obtained, the materials would have lower electrochemical surface area (ECSA). Even though this is disappointing, the achieved high activities of less controlled systems deserve high marks.
- This has been an ambitious project that aims to make a step-change in electrocatalyst design from current commercial materials. The project aims to directly address the DOE targets relating to electrocatalyst activity and stability. Arguably, the intent to take materials from inception to developed MEAs was overly ambitious, but this has proven to be a very solid project that tackles some very difficult issues.
- The project is directly addressing the barriers of catalyst performance, durability, and cost. The technical approach is novel in intentionally generating high-activity-alloy extended-surface catalysts rather than alloy nanoparticles, and it appears to be well executed and focused.
- The approach is focused on meeting the DOE targets to decrease Pt cost by decreasing its loading and increasing durability.
- This approach is based on existing systems that show very high activities and durability properties that should be able to overcome the barriers for automotive applications.
- The approach of this project is unique and tackles one of the key issues concerning catalytic activity and durability for the electrodes. The idea is innovative, and the impact would be significant if successful.
- This project has evolved over the years. Initially, there was great hope that by studying galvanic displacement on extended-surface substrates, nice continuous layers of Pt would be deposited. Having found difficulty in getting this to actually happen, a shift in focus to less crystallographically perfect Co and Ni core wires was understandably made, and the focus now has been to get these into operational cells before the program ends. The team should be congratulated on actually making devices, but it was done in an ad hoc manner. As a result, not much fundamental information about these materials was learned regarding what strategies to use to design next-generation catalysts other than to keep the surface area up and make them as active as possible. It would have been useful to have more information about the microstructure of the very high-activity catalysts. Their surface area is too high to be a transition metal alloy; for example, Pt/Ni catalysts usually have surface areas around 40–50 m^2/g. Unresolved is whether

the high activity is due to something intrinsic in the material or whether there is better accessibility of reactants. It would also have been useful, as an approach, to focus on the microstructure of how the catalyst is dispersed in the MEA catalyst layer; the microscopy resources of this program seem to be underutilized in this regard.

- The approach certainly has its merits, because it focuses on increasing available active sites on the catalyst. However, it is not clear how this would help reduce degradation, which is currently the main problem with catalysts. The degradation of Pt-based catalysts is well known, as are the reasons. The project aimed at increasing the utilization of available catalysts; however, it was not clear on how to solve the dissolution problem at high potentials and subsequent deposition at low potentials, leading to agglomeration of the particles and, consequently, performance loss. The data shown with the potential cycling test do show degradation within limits; however, degradation tests have to be more complete, because voltage cycling only does not provide certainty that the catalyst will be durable in an MEA under automotive conditions (e.g., including start-up/shutdown cycles).
- The approach to develop new catalyst materials is excellent. However, the schedule seems too tight regarding achieving performance/oxygen reduction reaction (ORR) targets in an MEA because there are a lot of barriers in the catalyst layer fabrication process. If the team keeps the schedule and target, it would be better to consider simultaneously what the critical challenges are for the selected materials to be an electrode and a scenario of how to overcome them.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- Remarkable progress has been made; materials have been developed that achieve four times the DOE 2020 mass activity target.
- The project team is to be commended for the depth with which it has looked to understand the materials that are being synthesized and to rationalize the activity and durability observed. This is apparent in the study of the role of the oxide within the Ni variant. It is, however, less than clear why such differences are seen in the Ni and Co systems. Although exceptionally high mass activities have been reported for some materials in the project, as determined from the summary “MEA and RDE data” slide, only a small number of the catalysts taken forward for MEA testing were seen to have met this target in rotating disk electrode (RDE) measurements. As is acknowledged, significant losses in moving to the MEA are observed; the reasons for this should be understood before spending extensive time on high current density operation. Good developments to higher-surface-area electrocatalysts have been made; this is considered integral to enabling tolerance to (even low levels of) the impurities required in real-world operation and, when MEA optimization is tried in earnest, good high current density performance.
- The observed increase in catalyst activity is certainly a merit of this project. It does show a potential route to increase beginning-of-life activity. The study on the oxide layer does provide good insights into the effect of oxidation of the catalyst. However, this was not the best area on which to focus the resources of last year. The effects of oxide layers on catalysts are relatively well known in the literature. They do provide protection for the nonoxidized part of the catalyst, but they are temporary layers that get dissolved again during low potentials. Over time, the nonoxidized part of the catalyst will be oxidized. The efforts would be better redirected if there were studies on how to prevent dissolved Pt particles from becoming detached from the ionomer and support as they are reduced under low potentials.
- The project team is commended on making excellent progress on developing high-activity catalysts, as measured by RDE. One critical point is that progress toward developing high-activity MEA electrodes is not nearly as advanced and remains a key barrier. In MEA, mass activities are lower than Pt/HSAC. The challenges of developing fuel cell electrodes with novel electrocatalysts are severe, and it appears this has not been as strong of a project focus as warranted. It is unclear if the team has a clear pathway toward resolving this issue. Assuming the electrode development issue can be resolved, another MEA integration challenge that must be addressed is the minimization of transition metal leaching in MEA, which negatively impacts rated power performance. Electrocatalyst durability of the highest-activity next-generation Pt nanowires (NGPtNW) against potential cycling must be improved. While the final mass activity is high, electrode loadings in MEA are determined to meet a minimum performance level at end of

life, and many of the higher-activity materials lost substantial fractions of their initial activity. Assuming the electrode development issue can be resolved, it is highly recommended that durability is evaluated in MEA form.

- The investigators made great progress in achieving high surface areas and specific activity catalysts and demonstrated high durability. They performed MEA optimization and achieved reasonable performance. The role of high surface area carbon (HSC) in the best-performing MEA is not clear. Its use is in contradiction with the initial carbon-free approach. The problem with metal leaching is the biggest obstacle at this point.
- Very good progress has been made toward increasing extended-surface catalysts' surface area, specific activities, and mass activities. Next-generation Pt nanowires look very promising based on RDE activities and fuel cell durability testing. It is still unclear if it is real to make both durable and highly active Pt-coated Ni nanowires. Ni nanowires are not stable when partially coated with Pt, and they are not very durable while fully coated with Pt.
- The rate of progress seems to be increasing as the project members have gained experience with these kinds of materials. It is disappointing that it has taken so long for them to translate "RDE expectations" into MEA performances. This is true, given the high levels of expertise of the personnel involved. This should imply that more understanding of electrode formation is needed, with less focus on screening lots of different ETFECS particle types and materials. Until the investigators understand how to make effective electrode structures that capture the advantages of the high-aspect-ratio thin-film ETFECS particles for ORR, they may not be able to correctly evaluate the latter. They should benchmark their MEA performances and durability results against the 3M-reported nanostructured thin film (NSTF) results rather than Pt/C, because the 3M results will likely have much better membrane integration and reveal whether they need to improve basic activity or electrode construction.
- It is commendable that the team made some highly active catalysts and translated them to MEAs, although their fuel cell performance was a bit disappointing. The team, however, did not learn much about the mechanism of high activity, nor the role of oxides.
- The team is continuously making progress, demonstrating that the 2020 targets can be achieved. However, it is still not entirely clear whether the issues associated with the oxide layer formed can be successfully addressed. This has been one of the concerns, and yet it remains uncertain.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The team is very strong covering synthesis; extensive characterization; testing; and finally, with addition of General Motors, consultation on fabrications of MEAs, which was the weakest point.
- Under this topic, the interaction with the partners seemed to have worked well. It was impressive that so many partners were involved in this project and that they managed to contribute in relevant ways to the successful areas of the project.
- This project features a well-coordinated effort between the National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory, Colorado School of Mines, and the University of Delaware.
- The researchers have a good mix of academics, original equipment manufacturers, and experienced suppliers.
- The project features very appropriate collaboration with partners, and each role is well defined.
- The wealth of ex situ analysis data clearly shows the roles of some of the other project partners, which are uniting to provide a cohesive study of this new material set. While the industrial partners will clearly not disclose too much information, more in-depth commentary on the feasibility of material scale-up would be helpful.
- Based on the publications, it looked like most of the work was performed at NREL and the input of the subcontractors was sub-par. The only publication with Yan (Delaware), for instance, was on Pt-coated copper nanowire in base, so it is only tangentially related to the project. In addition, the team did not address what it is doing with regard to the oxide layer.
- Collaborators have the appropriate skills to aid in the project mission. This year, it is not perfectly clear exactly which accomplishments could be attributed to a particular collaborator.

- The team's efforts are generally well orchestrated, but the role of individual team members is somewhat unclear.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The project is well aligned with Hydrogen and Fuel Cells Program objectives. The potential impact can be compromised by durability issues related to leaching of transition metals in an acidic polymer electrolyte membrane fuel cell environment.
- The project has advanced development of durable and active low-Pt-content catalysts. The accomplishments of achieving very high surface areas and high specific activities are advancing the overall progress in this development. There was incremental improvement in MEA fabrication and performance. The biggest problem is contamination with transition metal to improve durability.
- This project has a good shot at developing alternative catalyst approaches to the 3M NSTF technology that still relies on extended-surface-area catalyst concepts. Mass activities as measured in RDEs are promising, so the key areas that should receive focus include limitations of electrode fabrication with the team's catalyst approaches and whether they are amenable to high-volume manufacturability.
- The electrocatalytic process is one of the critical controlling factors for the performance of fuel cells. The project aims to develop a metal catalyst with unique structure that may improve catalytic activity as well as durability.
- The catalyst development portion of the project appears to be very successful and impactful toward generating high-activity ORR catalysts, a key commercialization barrier. If the high-activity catalysts can be integrated into fuel cell electrodes with similar activity, improved durability, and minimum base metal leaching, the technology could be revolutionary.
- The project could have a very big impact on further Pt reduction in the future. It achieved four times the mass activity by RDE compared to the DOE 2020 target.
- The main argument for relevance is scalability and the ease of using galvanic displacement. However, like any chemical reaction synthesis, it is not clear that scaling is easy. Indeed, it would have been useful to see how well a simple scale-up would do. It appears that the chemical vapor deposition (CVD)-grown nanowire templates are relatively "lower cost," especially compared to directly sputtering, or reducing similarly priced salts. Also, these materials have such a large amount of transition metal left that it is not obvious whether they can ever be removed. Passivating them behind or in an oxide will only last for so long, especially if the cell is cycled so that the cathode sees transient-reducing conditions.
- This project sought to directly address the DOE's key electrocatalyst targets and provide some real insights into some alternative ORR materials. As an extremely challenging project, it has not always achieved success, but this is exactly the type of fundamental materials project that should be supported. As the project concludes, it appears that its potential impact is one of learning and understanding, rather than of developing materials that will find a direct route to scale-up and application. This is in no way to diminish the outcomes of the project.
- The project addresses one of the key barriers, catalyst activity, which is relevant to the reduction of total Pt loading and further cost reduction. This has been obtained before with similar approaches, such as 3M NSTF, which does have performance problems at lower operating temperatures. It was not clear whether performance at wet conditions was also checked by the investigators here. Overall, this project is relevant in identifying new manufacturing methods to create structures that increase Pt activity, but this would be relevant in a future where basic durability issues are solved first.

Question 5: Proposed future work

This project was rated **2.9** for its proposed future work.

- The proposed future work is logical based on the current status. Optimization of fuel cell performance and evaluation of in-MEA durability are key and should be the primary focus of the project remainder.

- Although it is clear that very significant MEA optimization work is required to understand whether these catalysts are capable of giving the required operating performance, it is less than clear whether the project team and remaining project time will enable much meaningful progress to be made in this area. However, it is recommended that time and energy be spent on trying to understand why such a considerable drop-off in performance is observed in the move from RDE to MEA testing. Questions on material stability also remain. Owing to the use of transition metals capable of existing in both the metallic and oxide states, and also capable of leaching, it is suggested that durability studies utilizing oxygen, rather than nitrogen, would be prudent.
- The proposed future work states “Novel synthesis is focused on durability concerns of high performance transition metal containing materials.” This is the right direction; however, there has been no mention on what the approach would be to solve this problem. The transition metal materials used in the project so far (Co and Ni) have proved to have similar problems as Pt, with dissolution at high potentials. It is not clear how the synthesis will change this.
- The proposed future work is focused on overcoming the durability and stability issues identified last year. Revealing the role of graphitized carbon nanofibers in the structure of RDE films and fuel cell catalyst layers should be one of the priorities for the future work. While using an unsupported catalyst was one of the benefits of the proposed approach, incorporating carbon into the structure of the catalyst layer brings back problems with carbon corrosion and thickening the catalyst layer, among other issues, especially considering the high wt.% of carbon fibers used in RDE films, as reported in the 2014 American Chemical Society catalysis paper.
- The future work is correctly focused on the optimization of fuel cell performance, whereby good electrode fabrication will be the goal. But its downside is that it is still limited to making inks and dispersions. The researchers need to think outside the box and understand how to take full advantage of the high aspect ratio of the ETFECS particles and ways of packing them so that they realize the full mass activity potential. Studies of the MEA electrode losses to separate the mass transfer, ohmic, and kinetic losses are very good and should be done in-depth with dozens and dozens of MEAs using one type of catalyst and multiple controlled and varied fabrication/process variables. When the researchers progressively benchmark their best of class, they can do periodic durability testing.
- The future work is addressing all the relevant issues and challenges. However, with only a few months left, only limited progress can be made toward addressing the role and durability of transition metals. It is not exactly clear how MEAs will be optimized. The role of HSC must be addressed.
- Given the limited time remaining on this project, it makes sense to try to mitigate the effect of residual transition metals on performance.
- The proposed work identifies the remaining issues and suggests plans to address them. However, the proposed tasks are not entirely new, and it is not entirely clear whether the current issues can be effectively tackled by the work proposed.
- So far the progress is excellent in terms of material development. If the scope includes MEA performance, more detailed strategy and plans are needed.

Project strengths:

- The project features a strong team that has demonstrated an excellent capability to screen ETFECS electrocatalysts and achieve very high activity. The team has invested a lot into fundamental understanding of extended-surface area Pt catalysts, employing significant analytical characterization. The team has made significant progress toward fabricating electrode structures.
- The project combines advanced microscopic characterization techniques with well-established RDE and fuel cell characterization. Combined with synthetic intuition, it helps to make fast progress toward synthesis of catalysts with desired activities.
- A strength of the project is the galvanic displacement method that yielded higher beginning-of-life-activity catalysts. The down-selected synthesis method does have advantages such as a lower temperature for the synthesis, compared to alternatives.
- The team has developed novel approaches to generate catalysts with extraordinarily high activities in RDE. The project direction toward catalyst development has been logical and the team has proceeded with appropriate focus.

- Strengths of the project include the principal investigator (PI), collaborators, and experience of the group as a whole.
- The ideas of the project are unique and innovative. Progress is continuously being made, although it may not be fast enough.
- Strengths of the project include the potential impact of Pt reduction, measurement database and reproducibility, and management by the PI.
- This project has featured a very sound project scope and capable project partners, and it has been well coordinated.

Project weaknesses:

- The objective to make thick electrocatalyst layers to try and overcome some of the known water management issues with thin-film catalysts has been clear from the outset. While the reintroduction of carbons into the layer serves to achieve this, some of the known stability issues again come to the forefront. Clearly, the degradation of the electrocatalyst and the support medium are now separated, but carbon corrosion will lead to the same mass transport losses as occur in conventional layers. There is little discussion on the details of the materials that are selected to fulfill this role.
- The routes toward optimization of MEAs are not clearly defined. The use of HSC in a “carbon-free” approach is not expected.
- The project lacks a well-defined approach to increasing the durability of Pt-Ni nanowires. Using oxide films to prevent leaching of the transition metal does not seem like a promising solution because of (a) potential problems with conductivity and (b) the solubility of nickel oxide in an acidic environment.
- A weakness of this project is that the researchers are trying to force high-aspect-ratio, NSTF-type particles to behave in an electrode like a dispersed Pt/C catalyst.
- The progress on optimization of the catalytic activity is not very fast. The issues associated with oxide formation and its role are not yet addressed, and the plans to tackle these issues are not entirely clear.
- The MEA preparation strategy is an area of weakness.
- A research focus on the oxide layer is not key to solving durability problems.
- Fuel cell electrode performance is poor, and insufficient focus has been expended in this effort.

Recommendations for additions/deletions to project scope:

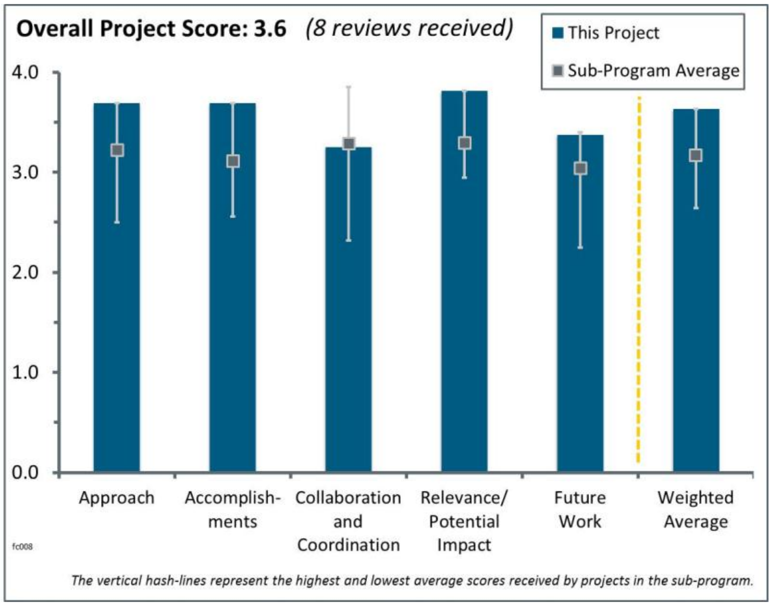
- The researchers should delete the oxide layer investigation. Performance of transition metal has been extensively researched by academia and industry. Failure modes, such as leaching and temporary sulphonic group exchange in the ionomer, have been extensively studied. The researchers should include start-up/shutdown durability testing (as based on relevant accelerated stress tests [ASTs]), and other automotive-based ASTs.
- This project should focus on material development. (The reviewer understands that 0.44 A/mg Pt as MEA is a stretch target.) For MEA optimization, more time is needed to solve a lot of further challenges. That could be included among the activities for the next DOE project (funding opportunity announcement).
- The researchers should delete some of the new catalyst particle synthesis work and replace it with studies to understand how to make optimized electrodes with the best catalyst particles they have now. Until this is done, they will not realize the maximum potential of any of their catalyst particle approaches.
- The effect of morphology on performance and leaching of transition metals is of great importance and must be studied.
- More significant progress should be made to address the remaining issues regarding the durability of the catalyst, and the results should be demonstrated.
- It would be beneficial if this project had a modest amount of additional time to specifically focus on electrode development to determine if there is a path forward.
- Not applicable—this project is scheduled to end in September 2014.

Project # FC-008: Nanosegregated Cathode Catalysts with Ultra-Low Pt Loading

Vojislav Stamenkovic; Argonne National Laboratory

Brief Summary of Project:

The main focus of this project is the development of highly efficient and durable multimetallic Pt-alloy nanosegregated catalysts for the oxygen reduction reaction (ORR) with ultra-low Pt content. Argonne National Laboratory (ANL) will establish a methodology capable of determining nanosegregated Pt-skin surfaces for different classes of electrocatalysts, as well as establish protocols for scaling up production of catalyst materials.



Question 1: Approach to performing the work

This project was rated **3.7** for its approach.

- The synthetic results, characterization effort, and achievements in specific activity and mass activity are excellent. The contributions into the fundamental structure-performance of catalyst structures are of great importance to the whole fuel cell community.
- The project has a strong focus on achieving targets well above the stated DOE technical targets, with the goal of achieving thin film Pt_3Ni activity. The systematic approach is focused on developing a knowledge base on the atomic structure relationships with catalyst activity and durability. The focus on catalyst targets, without diluting efforts of membrane electrode assembly (MEA) integration, is appropriate for catalyst work at this level.
- The Stamenkovic/Markovic group is truly an asset to fuel cell development. The group's research approach is effective, as shown by the advances it has made in exceeding DOE fuel cell technical targets. The project team is strong and well led.
- The materials-by-design approach to synthesize, understand, and develop the multimetallic nanoparticles in different structures is excellent, and the results prove this.
- The team has made significant progress toward the DOE goal. The experimental approach is reasonable and the results of the data analysis look convincing.
- Prior to this project, thin films of $Pt_3Ni(111)$ were found to have 90 times greater specific activity than Pt supported on carbon. This project has been an ongoing attempt to translate this finding into a practical nanoparticle catalyst that would be suitable for high-volume production. The project has expanded its scope in a productive manner. Rather than fixate on obtaining a high-activity PtNi nanoparticle, the team has also explored alternative morphologies (Pt alloy nanowires and mesostructured catalysts), the use of gold inner layers for stabilization, and PtNi nanoframes. The team has attempted in the past to scale up high-activity materials into quantities sufficient for cell testing; the same approach will be taken with the nanoframe catalysts.
- The researchers' approach is to try to get the $Pt_3Ni(111)$ surface into nanoparticulate catalysts using whatever options they find. In truth, the approach has been somewhat serendipitous and a bit ad hoc—last year they focused on annealed nanostructured thin film (NSTF), and this year they focused on the nanoframes. The results have been impressive but limited to laboratory scale. A recent focus on stability has been commendable, and the addition of ionic liquids into their materials is very interesting. One particularly good aspect of their approach has been careful microscopy to really understand the microstructure of the catalysts they are making.
- Focus should be on the crystalline phase of the surface to enhance the specific activity.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.7** for its accomplishments and progress.

- The project has made outstanding progress toward DOE goals. All technical targets have been met or exceeded. During the last stage of the project, high stability (exceeding that of Pt/C catalysts) was achieved.
- The project team has made strong progress and exceeded the DOE fuel cell goals for catalyst mass and specific activity. The team has met its performance goals with several Pt-alloy nanocatalysts and has shown good progress with its core-shell materials. The work in Pt-Ni nanoframes is very interesting. The Pt-alloy nanocatalysts have shown durability and are ready to be evaluated in MEAs.
- This project tackles one of the key issues that should be addressed to develop an electrode catalyst containing less Pt based on synthesis of a new type of macrostructure. The concept of the nanoframed catalyst is innovative, and the results of the activity test look promising.
- ANL has demonstrated outstanding accomplishments and progress. The focused approach is paying dividends with progressive improvements in catalyst activity through creation of new structures. In addition, excellent stabilization of particles has been achieved through the use of an Au interlayer. The nanoframe structures with the ionic liquid are an exciting development and provide a breakthrough in catalyst activity.
- This project features several outstanding outcomes, including the nanoframe catalyst.
- While cell testing is still awaited, this project has delivered the most important result for the entire Fuel Cell sub-program section of the 2014 DOE Hydrogen and Fuel Cells Program Annual Merit Review: a manufacturable nanoparticle catalyst that demonstrates 35-times activity improvement over Pt/C based on rotating disk measurements. No change in activity was found for nanoframe catalysts after 10,000 0.6–1.0 V cycles. Again, fuel cell testing is needed, as well as 30,000 cycles, but this is a good start. A small amount of Au was shown to retain mass activity of the PtNi nanoparticle after 10,000 0.6–1.1 V cycles. This may prove to be important to address eventual failure modes in PtNi catalysts. The project features an excellent use of characterization to confirm the existence of the Pt nanosegregation at the surface of the nanoparticles.
- Accomplishments in RDE are superlative, but not having MEA performance is discouraging. Mesostructured thin film (MSTF) has shown some promise in MEA, but many of the designs/catalysts systems are not tested in MEA, or at least not reported. Efforts should be made to realize the great RDE activities in MEA—that would be a breakthrough. A 30-times activity improvement with nanoframe over Pt/C is excellent, but the big question is how much one can expect in MEA. Even a 3–5-times improvement would be great in MEA. At the end, these catalysts need to work in MEAs. Excellent durability has been demonstrated under 0.6–1 V cycling, which is very promising.
- The development of new, highly active catalysts is impressive, and the characterization and modeling milestones will certainly be met. Less obvious is the progress toward the goals of integration into MEAs, much less scale up. These issues were marked as 70% and 55% complete, but the basis for these numbers is unclear.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The project features excellent collaboration between the partners. This is very evident from the work accomplished, publications, and patents.
- There has been good collaboration with other national laboratories (e.g., the microscopic analysis with Oak Ridge National Laboratory [ORNL]) and industry (3M).
- The Stamenkovic/Markovic group has excellent interaction with other institutions and has led the project team well.
- Collaborators are listed to be ORNL (microscopy), the University of Pittsburgh (theoretical modeling), 3M (MEA testing), General Motors (GM) (technology transfer), and Brown (synthesis). Judging from the slides presented on just the past year’s work, it is difficult to see where significant collaboration existed. It appears that ORNL contributed to the microscopy, particularly in terms of identifying composition versus

position over an individual nanoparticle. Theoretical modeling and MEA testing did not appear to play a significant role in the past year's achievements, so there is not much mention of the University of Pittsburgh or 3M. Given the degree of accomplishment in the past year, however, the investigators may not have needed these collaborations at this stage in the project. However, MEA testing should happen soon now that RDE testing has yielded some outstanding results. It is difficult to say whether Brown University played a role in the past year's work. For future reporting, the project may wish to adopt the convention of another ANL project and place logos to show which collaborators worked on which tasks.

- The microscopy collaboration with ORNL has been excellent, as has been the interactions with 3M. The interactions with the Brown University and University of Pittsburgh groups have been less obvious over the past year, and the nanoframe work was done with the University of California, Berkeley, which was not recognized as a collaborator.
- Individual team efforts are well orchestrated to maximize the synergy among the collaborators. However, the role of GM seems to be less clear.
- The project team features suitable collaboration, with industry, universities, and national laboratories represented. Better identification of the relative contributions of each team member would be useful.
- The collaborators' roles are well defined on slide 23 but not very transparent from the overall report.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.8** for its relevance/potential impact.

- Cost analyses over the past 3–4 years have shown that the projected cost of a fuel cell system has hit a plateau in the range of about \$53–\$56/kW. DOE must fund efforts to reduce costs significantly. The most direct way to do this is to improve catalyst activity, which should result in an improvement of the polarization curve that drives down the area of the stack, resulting in less Pt, fewer membranes, fewer gas diffusion layers, and fewer plates. ANL has discovered at least two catalyst systems that significantly increase oxygen reduction activity. The project has explored catalysts with materials that are commonly used for manufacturing. Nickel nitrate is commonly used in industry and is handled safely. Reaction time to make the solid polyhedral nanoparticle is only three minutes. Lowering the cost of balance-of-plant components and some stack components often does little but lower the cost of an individual component. A project like this, which vastly improves catalyst activity, can lower the cost of the entire stack and also improve performance under lower pressure, which could reduce balance-of-plant component cost. The results of the project could be used to improve the entire system.
- The project has focused on developing different design platforms of multimetallic nanoscale catalysts that are highly relevant to advancing the commercialization of fuel cells. The nanosegregated Pt alloys demonstrated high performance, durability, and scalability potential. The nanoframe structures demonstrate exceptional specific activity and mass activity, but their scalability is under question.
- This project is very relevant to the issues of cost, performance, and durability being addressed by the Fuel Cell Technologies Office. This project has the potential to surpass DOE's research and development goals under realistic MEA conditions. Charts show that it has already surpassed DOE's target, although in RDE.
- The team has really made excellent progress on delivering a vision of new catalyst materials for oxygen reduction. New paths forward with regard to the synthesis of new materials and incorporation of the ionic liquid speak to exciting new directions.
- The use of Pt as a catalyst has been a major issue in developing fuel cells. This project aims to develop a catalyst with a novel structure that enables less use of Pt. The team members shed light on a basic understanding of ORR, a key process for electrocatalytic reactions.
- The project is extremely well aligned with the DOE Hydrogen and Fuel Cells Program (the Program) goals and with the need for step-change improvements to Pt catalysts. The dual approach of high durability and very-high-activity catalysts provides a real path to low-cost fuel cells.
- Enhancement of ORR activity is one of the most important areas on which to focus.
- The research being led by the Stamenkovic/Markovic group is critical for meeting the Program's goals.

Question 5: Proposed future work

This project was rated **3.4** for its proposed future work.

- Future work points toward MEA testing of the catalyst in a fuel cell, which is needed in order to understand what the catalyst does in a cell environment and to begin gaining some understanding whether special processes (ink, application, pressing, etc.) are needed throughout the process of integrating the catalyst. MEA testing is also needed to understand the robustness to temperature, humidity, and transient operation. Most importantly, it is also needed to understand durability. It may also be interesting to follow up on further cell testing of the MSTF materials reported last year. A polarization curve was shown last year with MSTF that could possibly be improved if efforts were taken to address high current performance. Cell testing of catalysts with Au inner layers (especially accelerated stress tests) would also be useful to understand if the same trends from rotating disc experiments exist in a fuel cell.
- Considering that the project is ending, the future work is very relevant, particularly the MEA testing of nanoframes and scaling up of the synthesis approach.
- The future work is very well outlined with a focus on evaluation in MEA and scaling up to produce larger quantities.
- The Tafel slope is an important factor to evaluate the cathode catalyst.
- The future work is appropriate. The approach to date to focus on the catalyst structure and development of catalyst design knowledge for high activity and durability in a Pt-thrifted catalyst is appropriate. The project is now at the stage where increased focus on exploration of synthesis scale-up and preliminary MEA testing should be conducted.
- Per the “Future Work” section of the progress report, the team is focused on continuing catalysts optimization and scale-up. The materials seem to have reached a maturity where incorporation into MEA is required to assess DOE goals.
- The future plan focuses on a mechanistic understanding of the ORR reactions using the new nanoframed catalyst as well as the core-shell structured catalyst. On the other hand, the applicability of such a catalyst seems unclear.
- Incorporation of these catalyst materials into an MEA should be a priority for this team during the next year.

Project strengths:

- The efforts to improve catalyst activity are the most relevant work to the DOE fuel cell portfolio. The approach to develop nanoparticles that take advantage of high-PtNi specific activity through nanosegregation of Pt at the surface is a natural progression from prior breakthroughs and has sufficient scientific foundation. While the project is derived from prior work, it has also addressed challenges with immense creativity (e.g., nanoframes, MSTFs). The project has some of the very best RDE scientists involved in the measurements. In general, the project makes use of an all-star team of electrochemists.
- The project team has maintained a disciplined and detailed approach to develop structure-function relationships for high-activity, durable catalysts to maximize the use of noble metals. Strengths include in-depth theoretical understanding, catalyst synthesis, and material and electrochemical characterization.
- The Stamenkovic/Markovic group has worked hard to make this project successful. The catalysts development approach has been executed very well. The coordination with other team members is also a strength. The Pt-alloy catalyst technology is very mature and the durability seems excellent. The group seems to have progressed very well toward exceeding the DOE technical targets.
- ANL demonstrated outstanding synthetic capabilities. The contribution into structure-property relationships of different types of structures is of great importance. Different classes of materials demonstrate activity and durability superior to Pt/C.
- Strengths include the ANL team, ORNL, and collaborators; the material-by-design approach; the characterization techniques; and the excellent and accurate RDE evaluations.
- Strengths of the project are its focus on a pseudo-bulk and surface crystal orientation of catalyst concept to enhance ORR activity, and its effective collaboration with high-resolution microscopic analysis.
- The project features a strong, chemistry-based, innovative design of the catalyst, which enhances the catalytic activity for the ORR, leading to less use of Pt.

- This project features very-high-performing catalysts and novel directions for catalyst design.

Project weaknesses:

- Greater emphasis could be made on fuel cell testing versus RDE testing, especially now in the later stages of the project. The 3M and GM collaborations need to work better. The 3M MSTF polarization from last year may have sold the catalyst short, given the high activity. There should be some way to capture the activity of the catalyst in situ and have polarization curves that avoid major mass transport losses from as low as 1.0 A/cm^2. In general, the project needs to make better use of the non-ORNL collaborations. The best work appears to come from within ANL, but other partners could contribute more.
- There is almost no MEA evaluation, and there is too much focus on RDE data. MEA performance and durability are different and many things can be learned from MEA testing that can help in designing a stable and high-performing electrocatalyst. In addition, the researchers are synthesizing too many designs/structures instead of down-selecting one and putting efforts into making it work in MEA.
- As with many catalyst development tasks, a stronger focus on MEA development is needed. If it is difficult to transition the catalysts to MEA operation, the ultimate DOE goal of commercializing fuel cell technology may not be met.
- The optimization of MEAs of Pt alloys is not sufficient. The scalability and cost of synthesis of nanoframes is the biggest barrier at this point.
- The application of such a catalyst to fuel cell systems is still in question because of several issues, including the cost for the synthesis and scalability.
- The project features an ad hoc approach to materials discovery. The full team involvement is not clear.

Recommendations for additions/deletions to project scope:

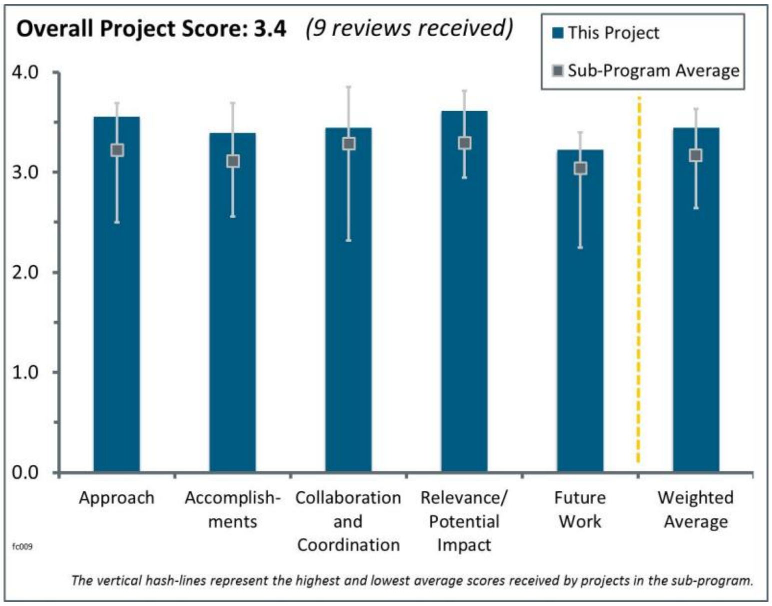
- The work is excellent. The only recommendation is to focus on the MEA development. The reviewer is looking forward to seeing the fuel cell/MEA performance with these novel catalysts.
- Instead of developing any more new structures, the team should focus on how to realize the great activities in MEA with the current designs. It may not have the same improvement as in RDE, but any improvement in MEA will help the research to progress further.
- Promising outcomes of cathode catalyst materials can be seen. High performance of mass activity at MEA (rather than RDE) is expected, particularly for the nanoframe concept. Significant progress on the MSTF concept—which was presented in 2013—was expected because the manufacturing process is promising (already demonstrated by NSTF at 3M).
- Officially, the project only has three months left. Emphasis should be on fuel cell testing with the nanoframe catalyst, and in that, there is a lot to do. The team could add fuel cell testing on the Au inner layer catalysts, as well as another try with MSTF.
- The scalability and manufacturing of the catalyst with performance data should be provided.

Project # FC-009: Contiguous Pt Monolayer O_2 Reduction Electrocatalysts on High-Stability, Low-Cost Supports

Radoslav Adzic; Brookhaven National Laboratory

Brief Summary of Project:

The overall objectives of this project are to: (1) synthesize a high-performance Pt monolayer (ML) on stable, inexpensive metal or alloy nanostructure fuel cell electrocatalysts for the oxygen reduction reaction (ORR), and (2) increase the activity and stability of the Pt monolayer shell and the stability of the supporting cores, while reducing noble metal content. Project objectives for the current review period include: (1) scale up of syntheses of three catalysts, (2) obtaining perfect Pt ML deposition and achieving 100% utilization of Pt, (3) developing new methods for increasing the stability of core-shell nanoparticles, and (4) delivering a 300 cm^2 membrane electrode assembly (MEA) for testing at General Motors (GM).



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.6** for its approach.

- This project's core-shell approach has proven to be one of the most fruitful pathways toward lowering platinum group metal (PGM) costs in polymer electrolyte membrane fuel cells (PEMFCs). The continued efforts toward the use of non-noble-metal cores, now through nitridation of base metals, gives a pathway to significant further cost reductions and should be emphasized in future work. Brookhaven National Laboratory (BNL) should continue on the path to move away from reliance on rotating disk electrode (RDE) testing toward more demonstrations in MEAs. Work with currently inexpensive, but scarce, PGMs such as Re should be limited, as any substantial use of such metals in mass production would drive their prices up, potentially above that of Pt. Rhenium does seem to have an advantage in that it is generally extracted from different rocks than those that yield Pt and other PGMs. Efforts toward more manufacturable methods of making catalysts should be continued (e.g., reactive spray and scale-up of electrodeposition on powders). Direct electrodeposition on gas diffusion media is unlikely to be practical in mass production.
- A core-shell approach with a perfect Pt ML on cheap cores is a very good approach. It has the potential (also demonstrated already) to reduce Pt loadings. Technology transfer to industry would also address the scale-up issues.
- The Adzic team has been a leader in developing the core-shell approach to fuel cell electrocatalysts. It is very relevant that the team is able to reproduce these samples on a large enough scale to be tested in multiple laboratories.
- The approach of Pt ML catalysts is tackled in this project with great focus. The synthesis strategy is clear and has led to many new materials being developed. BNL has a keen awareness of the technical difficulties in scaling up the process, but it has devoted the proper amount of time and attention to this issue, working with industry and other collaborators.
- BNL uses innovative technology to develop low-PGM catalysts. Previous results on Pt-Pd cores have been very encouraging in the laboratory and have been scaled up for commercial evaluation. The new approaches are mostly electrodeposition based; however, plasma processes are now being developed to reduce cost.

- The methodology was invented at BNL and has since been verified at many places. BNL continues to innovate in this area and is making good scientific progress. The stability of the core materials is still a major concern, but some approaches have been laid out to address it. More evaluation in an MEA is required to differentiate good approaches from bad ones. That being said, the project has a more practical approach than most projects—showing transferrable technology from RDE to MEA and successful technology transfer to a catalyst supplier.
- The approach is focused on U.S. Department of Energy (DOE) targets to lower noble metal content and reduce the cost of the cathode catalysts in PEMFCs.
- The focus is on a novel concept of core-shell to realize a pseudo-bulk catalyst concept for both nanowire and nanoparticle.
- This year, BNL appears to have made good progress toward the development of low-cost, high-stability Ni4N cores while largely maintaining high specific activities, which has resulted in a good step forward for the project. Too much time was spent on catalyst development with Pd-based cores. While it was very important to use such materials in the concept demonstration phase, development work with PGM cores should be de-emphasized because of cost considerations. Evaluation of performance and durability at the MEA scale still appears to be rather limited. While the newly developed materials have very good activity and durability in RDE, MEA demonstration is critical and needs to be a larger focus now that non-PGM cores are available.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.4** for its accomplishments and progress.

- Excellent progress has been made toward synthesis of highly active catalysts with low total PGM content. New, more stable cores—versus those of pure transition metals—were identified and synthesized. Much faster progress has been achieved in RDE testing versus fuel cells.
- Excellent progress with MEA evaluation was made by industry partner GM. High activities and very good durability have been demonstrated with the 0.030 mg Pt/cm^2 loading cathode. Air performance is poor, but suggestions were made that can improve it. It would be nice if the team showed some Pt/C benchmark data with similar Pt loading on the same plot to get perspective on how much improvement there is due to the core-shells.
- BNL is commended for reporting both transmission electron microscopy (TEM) and x-ray diffraction (XRD) data of its samples. Few researchers in the field do this, because the XRD is an average measurement; they cannot pick and choose areas of the TEM samples that support their conclusions. BNL investigated a number of bimetallic systems and worked with fuel cell developers to obtain fuel cell testing data. The nitride core work is also very interesting.
- BNL has delivered outstanding outcomes. Progress from last year is not as good as from previous years. It is good to evaluate ORR activity at the MEA level as well as in RDE.
- Good progress has been made, considering the project mostly ended. It was encouraging to see the application of Ru-Pt catalyst in an electrolyzer's hydrogen electrode. MEA activity measurement is often done at high oxygen partial pressure, which skews the activity higher. The principal investigator (PI) should comply with the DOE-recommended protocols.
- The project appears to have made a substantial step forward with the Pt ML on Ni_4N core system in terms of cost reduction.
- BNL continues to make new advances. The accomplishments over the past year are noteworthy because they include new concepts for generating active fuel cell catalysts.
- The team has primarily focused on stability and has been able to demonstrate impressive stability of its materials by taking advantage of interesting nanoscale effects. Significant increases in mass activity seen in RDE are being translated into MEAs.
- Several novel catalysts demonstrated total PGM mass activities comparable to more conventional Pt alloys—some using metals currently cheaper than Pt. BNL continues to demonstrate improved control over the composition and structure of particles at the atomic level. BNL demonstrated improved uniformity of the particles. There has been no further work on the promising hollow Pt particles discussed in past years. While the activity of those per mass Pt was not as high as those for the systems that have received follow-up, they were still promising in activity and are more likely to give adequate durability than those containing less-corrosion-resistant PGMs, such as Pd.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- There is excellent collaboration under this project. There is a strong team and strong interaction with industry. MEAs are tested by industry partner GM.
- A number of partners are actively participating in this project. It is good to see the contributions from theory and the testing of the materials at GM and other industrial partners.
- The interactions with industry (i.e., MEA and scale-up) and with the University of Wisconsin (UW) (i.e., theory and calculations) seem fruitful.
- Work is well coordinated with scientific and commercialization partners. The leveraging of DOE Office of Basic Energy Sciences funds and research activities for studying fundamentals is also well coordinated.
- This project is an excellent model of technology transfer to the industry through licensing.
- BNL actively seeks feedback from original equipment manufacturers (OEMs) and makes efforts to improve. This project is one of the most practical projects and shows great potential to contribute to the marketplace. However, it appears that most synthesis and characterization work was done at BNL. Collaboration with others is limited to testing. More collaboration in other areas will benefit this very promising approach.
- The project features very good collaboration between BNL, Michigan Technological University, and University of Wisconsin. More extensive collaboration with industrial partners would be helpful.
- Collaborators made a good start on MEA testing; such activity should be emphasized in the future. If possible, an update on development progress at the licensees of the patents from this project (e.g., N.E. Chem Cat Co.) should be given at DOE reviews. Reactive spray deposition is an interesting approach, but it is so different from the methods used at BNL that the relevance to the core of the project is unclear.
- The role of most collaborators appears rather limited. It is unclear what contributions, if any, were made by Johnson-Matthey Fuel Cells Inc. and Toyota, for example. The project would benefit greatly from having a dedicated development effort to optimize fuel cell electrodes.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.6** for its relevance/potential impact.

- This project has led the development of core-shell catalysts that constitute one of the most promising pathways to the reduction of Pt usage in PEMFCs. Reducing Pt costs is one of the critical goals needed to enable use of fuel cells in mass-produced applications. By providing high-PGM mass activities in catalysts with high specific surface areas, core-shell catalysts provide a pathway toward addressing the problems in high-current-density operation in air that have typically been seen for low-loaded catalysts.
- Considering the high activities of low-PGM catalysts toward ORR, the project has the potential to significantly advance DOE goals toward commercialization of PEMFCs.
- This project has made a significant impact in realizing DOE research and development goals, and industries are interested in the technology.
- The work to develop stable, high-activity, and low-cost electrocatalysts is of key importance to the DOE Hydrogen and Fuel Cells Program.
- The work is extremely relevant to meeting the DOE goals of reducing catalyst loading in fuel cells.
- Enhancement of ORR activity is one of the most important technical focuses to fill the gap.
- Novel catalysts are essential for achieving DOE goals; however, it is unclear whether the added costs of adding the other metal components are fully considered. A full cradle-to-grave assessment of the costs and the environmental impact in terms of waste products produced during synthesis should also be considered as the methods continue to be perfected. Large-scale industrial manufacturing may be precluded due to some of the more expensive rare earth elements being considered.
- Although the team has shown that its catalysts are active and durable, at least in research settings, the catalysts still seem very complicated to make. As such, how much impact the team’s methods will have

remains to be seen. That said, the team is trying creative variants to the problem, including electrodeposition and reactive spray deposition, and it may overcome this issue.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The future work plan makes sense for the continued optimization of the low-loading PGM core-shell catalysts.
- The MEA and stack testing at GM is a very promising step.
- The future work is well balanced. Durability tests need to be complemented by tests under "start-stop" conditions (i.e., between 1 and 1.5 V).
- The plan for the proposed work shows new concepts such as the onion ring structures, which may be interesting candidates. The economics of producing such structures need to be considered, both from a materials perspective and in terms of the possible waste products being generated during synthesis.
- The team is guided by good modeling efforts. One of the things BNLwould like to do is incorporate Y into its materials. This may be quite challenging, and technical barriers were not discussed.
- The team should continue the trend toward MEA testing and away from total reliance on RDE. MEA testing should include rigorous durability testing, as even metals as noble as Pd can cause major problems in fuel cells subjected to such tests. If nitrided base-metal cores show any real promise in RDE tests, MEA testing plans should include such catalysts. The effort to be expended on the promise of PtY and PtSc alloys (based on theory that neglected the severe problem of oxidation of Y and Sc) should be limited. Nonaqueous solvents and possibly thermospray are more promising approaches than any aqueous processing method, but the chances of such alloys being stable in fuel cell applications are very low. Straight vacuum deposition would seem to be a better approach if these materials need to be studied. If DOE funds are to be spent on these systems, it would seem to make the most sense for DOE to pay 3M to grow some PtY and/or PtSc nanostructured thin film at the 50 cm^2 scale.
- The project is ending. MEA testing should be included for all new catalyst work as a means to evaluate stability. As shown by many, catalysts with acceptable activity and stability in RDE often do not show the same properties in MEAs. More effort on materials that are valued by suppliers and OEMs should be made.

Project strengths:

- The PI has a vision of how active catalysts should be designed. This helps to synthesize highly active catalysts in a timely manner. In addition, the strong theoretical component provides fundamental insights on how the catalysts work.
- Strengths include the very strong team that made lots of MEA evaluations under O_2 and air, the strong collaboration with an industry partner, and the efforts to move forward with stack testing.
- The project features a novel concept of core-shells to enhance ORR mass activity significantly. It also features an excellent technology transfer model with industry partners.
- Strengths include the strong technical capability, a good record on practical invention, and healthy motivation toward commercialization.
- This project is a leading-edge electrocatalyst development effort with strong modeling, and ex situ and in situ characterization capabilities. An active effort to reduce the PGM content of cores is critically important.
- This is a very-well-managed project that continues to produce excellent results.
- The approach is multidisciplinary and is performed by extremely knowledgeable researchers.
- The project features impressive control of the deposition of multilayer nanoparticle catalyst systems. In addition, it features very impressive initial kinetic activities expressed per gram of Pt. The initial kinetic activities per gram of total noble metal or per unit metal cost at projected mass-production volumes are less impressive, but still encouraging. There is good coordination between synthesis and characterization.

Project weaknesses:

- One weakness is the continued reliance on RDE testing of ORR activity and, even more of a concern, for durability information.
- Direct electrodeposition onto gas diffusion media is unlikely to be feasible in mass production. While advanced catalysts on support powders can be dropped into fuel cell projects, catalysts electrodeposited onto gas diffusion layers would likely require extensive reengineering of fuel cell systems to give robust performance over such operating conditions as cold start-up and load transients.
- The PI is encouraged to utilize the U.S. DRIVE Partnership's Fuel Cell Technical Team durability accelerated stress tests and polarization curve protocols to allow for direct comparison to other projects. Too much focus continues to be placed on work with solid precious metal cores.
- It would be nice to see the high stability of the core in the case of the nitride-stabilized Pt-M core-shell catalyst in MEA. A benchmark against commercial Pt/C or PtCo/C with similar Pt loading was missing.
- Weaknesses include the inconsistency of MEA activity measurements and the high dependency on the use of PGM for a sufficiently stable core.
- MEA tests are needed to demonstrate the broader applicability of this work.
- The Pt ML is not very durable, as has been shown before.

Recommendations for additions/deletions to project scope:

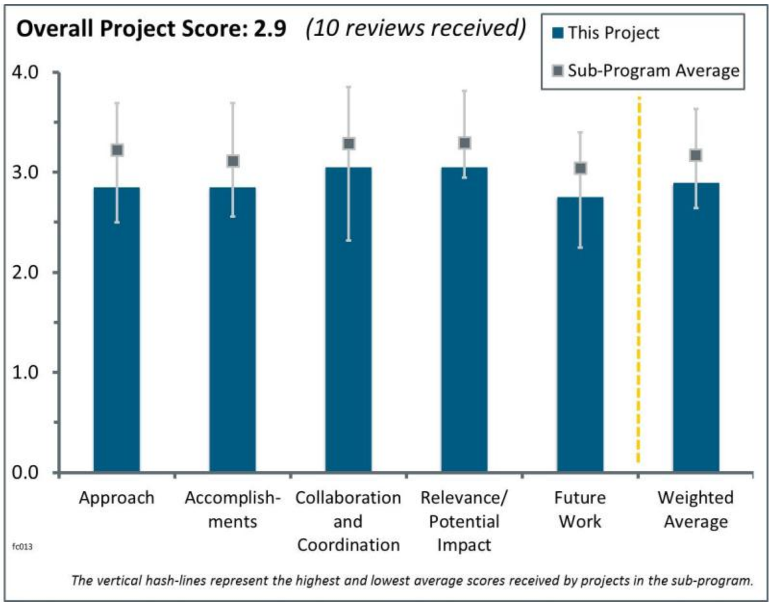
- Pure transition metal cores should be excluded from the scope; it has been shown multiple times that they leach. The issue of stability of ML Pt or mixed ML film in fuel cell tests needs to be addressed. It was reported by the Argonne National Laboratory team at last year's DOE Hydrogen and Fuel Cells Program Annual Merit Review meeting that three MLs of Pt are necessary to keep the shell stable in fuel cell tests.
- BNL should comply with DOE-recommended protocols. The team needs more understanding of the fabrication cost with the electrodeposition approach.
- Dedicated effort to integrate electrocatalyst into high-activity electrodes is a critical next step to validate the performance and durability observed in RDE.
- BNL should consider leaving PtY and PtSc to folks experienced with vacuum deposition. It should also work with OEMs to optimize core-shell catalysts for high-current-density performance in H_2/air.
- Improvement in air performance would be good.
- The hollow core-shell concept was expected to see progress.
- Catalyst costs need to be evaluated.

Project # FC-013: Durability Improvements through Degradation Mechanism Studies

Rod Borup; Los Alamos National Laboratory

Brief Summary of Project:

The objective of this project is to improve fuel cell durability without compromising component cost or performance. Los Alamos National Laboratory (LANL) will identify and quantify degradation mechanisms through characterization of the impact of component interactions, operating conditions, and electrode structure on durability and performance. Methods to mitigate degradation of components are investigated, and degradation mechanisms are used to design new materials and develop operating strategies. Models are developed relating components and operation to fuel cell durability.



Question 1: Approach to performing the work

This project was rated **2.9** for its approach.

- The project features a strong combination of characterization, diagnostics, and modeling, which is beginning to extrapolate the impacts of degradation on lifetime.
- The approach is generally good and addresses the known issues of durability in polymer electrolyte membrane fuel cells (PEMFCs). In some areas such as the electrochemical impedance spectroscopy (EIS) plots in slide 21 and 22, it is not clear if data are presumably taken under O_2 or air. Data taken under N_2 would provide the change in the catalyst layer resistance that is critical in estimating the change in catalyst layer thickness. The particle size distribution change (growth) with durability as a function of the type of carbon black has been well established for the last decade, and it is not clear what is new in that area from the presentation. Ce has been shown to be effective in recent studies by automotive companies when used in small quantities, and it does not leach out as badly as presented in this work. Mitigation has been addressed in this work, which is good, but most of the mitigation technologies for shutdown/start-up (SD/SU) have been patented by the automotive companies and are easily available. These mitigation technologies are being implemented in the next generation of fuel cell electric vehicles. It is not clear why these patents are being ignored and not studied in detail. The automotive companies are ahead of the national laboratories in this area, and it would be a good approach to study the mitigation techniques that actually work and bypass the need for durable supports. Perhaps a different group or laboratory should be funded to summarize these mitigation techniques.
- The approach is mostly a post-mortem approach—trying to simulate fuel cell operating conditions or obtain as much material from industry as possible and then figure out what went wrong. While this is a defensible approach, it is always a few years dated; materials change and often what researchers are looking at is no longer relevant. Cathode carbon degradation is a clear example; the original equipment manufacturers (OEMs) have suggested to decrease emphasis here because they have mitigation strategies with which they are content. Where the national laboratories can be most useful is chasing down mechanistic studies; for example, the investigators found that Ce doping ends up in the cathode and anode and leaves the membrane electrode assembly (MEA) altogether. There are questions about why it leaves, what counter ion it left with, and why it segregates in the catalyst layers. The investigators can only guess; a very simple experiment using a Pt black electrode would determine if it was catalyst affinity or carbon affinity that was

sequestering it there. If carbon; there are questions about whether a carboxylic functional group is leading to the capture, and whether carboxylic acids have a higher affinity than sulfonic acids. These are all simple experiments that could aid the community, regardless of the membrane/catalyst system being investigated.

- Overall, this project is attempting to address key commercialization barriers due to insufficient durability of PEMFC materials. The project is well focused in terms of studying relevant degradation modes. However, this reviewer questions the relevance of exhaustive studies of carbon corrosion; Pt particle growth; and electrode thinning on outdated carbon-supported, pure-Pt nanoparticle catalysts, because these topics have been studied in depth for many years and it is clear they cannot achieve the performance or durability targets. Significant utility can be obtained from all this work if it results in the development of an overall degradation model that is predictive of performance as a function of time and degradation extent. While modeling is listed in the approach slide, little modeling appears to have been done, and few, if any, correlations of the component degradation extent to performance loss have been made. The results appear to be largely one-off tests without replicates. Sample-to-sample variability effects could be large. For example, the very unexpected result on slide 11, where the H_2 crossover increased substantially with *dry* SD/SU, should be repeated before any conclusions are drawn.
- The team is composed of respected groups from national laboratories and industries. The multidirectional approaches taken for the completion of all tasks are adequate. All the technical barriers have been addressed appropriately. However, the team has used MEAs composed only of Nafion® ionomer (in membrane and catalyst layers). The team should plan to sample MEAs that use different types of perfluorinated (e.g., 3M, Solvay) ionomers to broadly understand MEA degradation.
- The team is doing a limited set of durability tests combined with thorough, advanced post-mortem analysis, but it is not doing deep enough parametric studies (employing design of experiments) and diagnostics to provide the fundamental mechanistic learning that will help developers come up with effective degradation mitigation strategies. The researchers seem to run isolated sets of tests and then diagnose what kind of degradation is present, rather than actively address the critical degradation phenomena that are limiting (at least for light-duty automotive) fuel cell commercialization.
- This project has a huge scope; part of the approach should include sensitivity studies to organize degradation mechanisms in terms of expected mV lost at the end of life, and resources should be prioritized. Currently, it seems that resources are prioritized around available characterization methods.
- The project employs a combined modeling and experimental approach and coordinates activities with other durability projects.
- This project features a good approach based on extensive characterization and modeling, and it facilitates the development of mitigation strategies.
- The major problem with the approach in this project is that it overlaps with activities being pursued within automotive and fuel cell stack OEMs. Unlike LANL, the OEMs have access to state-of-the-art materials through non-disclosure arrangements and joint development agreements. Despite identification of an automotive durability target, there is no automotive OEM associated with the project. The different tasks shown involve Ce migration, SD/SU degradation, OCV degradation, and carbon corrosion. These phenomena are all well studied by OEMs. The best approach for the project is to discover experimentally new failure modes that have not been observed before. However, without state-of-the-art material sets and without OEM cell designs, the effort turns into guesswork. This is especially true when transient operating conditions (e.g., SD/SU) are also missing. The protocol for membrane degradation under SD/SU needs to be clearly reported. For a complete analysis of carbon corrosion, statistics for carbon loss, thickness loss, electrochemical surface area (ECSA) loss, and performance loss should all be rigorously compared. This should be done for both absolute numbers and percentages.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- The team has made great progress in defining MEA degradation mechanisms and, to some extent, providing mitigation conditions. The modeling of carbon corrosion and loss during SD/SU and expansion of the model for membrane durability is well done. The team has done a good job in identifying membrane and catalyst degradation mechanisms separately and offering mitigation strategies that are not at the expense of performance or additional cost. The team also has done a good job in identifying the Ce migration from the membrane to catalyst layers. The team should consider conducting the studies with MEAs with a Ce-containing membrane (such as Nafion®-XL) and Ce-containing Nafion® ionomers in the electrode layers to understand if the migration behavior of Ce occurs when there is no Ce concentration gradient between the membrane and catalyst layers.

- The presentation shows comprehensive studies on MEA degradation and mitigation with mostly qualitative analysis on cause and effect. The results of Ce migration from membrane to catalyst layers is interesting and disturbing, which warrants a quantitative study by modeling.
- The team has identified some new mechanisms and effects, as well as screened several mitigation strategies.
- The accomplishments are moderate, based on the approach adopted. Based on what is already known in the literature and in industry, new advancements in techniques or new insights are a bit scarce. Slide 11 does not have complete information on the plots, as is the case with several other slides. It is unclear if the ECSAs after the durability tests were measured at room temperature with 100% relative humidity (RH). The HUPD peaks look smeared, indicating that the conditions for the measurement of the ECSA were suboptimal. Low N_2 flow and 100% RH provide the best HUPD areas. ECSA values are not reported in units of m^2/g, so the base ECSA value is not known from the figures.
- Nearly all of the work presented for this year is on carbon corrosion. Very good work was done on the carbon corrosion modeling and tornado plot, which are very good and helpful; however, it is not clear how much of a problem carbon corrosion appears to be and this could be too large of an effort on a questionable problem. Only superficial work was done on Ce, where the team is capable of doing some very strong work; it has all of the capabilities.
- Good progress has been made toward evaluating the effects of carbon corrosion and load cycling accelerated stress tests (ASTs) on electrode and electrocatalyst structure, but it is questionable how useful this work is because the degradation of these materials has already been so well documented. Characterization of Ce movement in MEA and modeling of pinhole growth in polymer electrolyte membranes (PEMs) at Lawrence Berkeley National Laboratory (LBNL) are useful.
- The team has presented several examples of not-well-understood degradation results, which could potentially lead to misleading conclusions. For example, the start/stop testing results compared at dry and wet conditions could lead viewers to believe that anode purge during shutdown leads to accelerated membrane degradation. Because these results conflict with expectations, they warrant repeating with added diagnostics before dissemination. It was also unclear where SiO_2 particles came from in the OCV tests and why they were in the MEA in the first place. The work on decreasing cathode Pt weight loading compared to diluent carbon showed some interesting results, but without a mechanistic understanding, it does not drive the development of improved electrode designs. The catalyst layer porosity loss during the drive cycle was particularly interesting. This is one area where the results could drive developers to seek solutions as well as help in the development of performance degradation models, assuming the porosity change can be quantified and modeled.
- Results involving membrane degradation under SD/SU with dry conditions are somewhat confusing. It is unclear why membrane degradation would “level off.” This is rarely observed. Observations of Si-O particles may be particular to the membrane being used. It is interesting to see the cathode ionomer skin missing, but ionomer degradation on the cathode side has been reported before. Quick decrease in thickness and porosity due to carbon corrosion for Vulcan or high-surface-area carbon has been observed. Slower decrease in thickness loss for graphitized carbon has also been observed. Some interesting trends were shown: preference of Ce in catalyst layers, quicker Pt particle growth for graphitized carbons (and then no more), ionomer removal over channel regions during OCV testing, and inclusion of residence time in the SD/SU model (could be used as a way to translate to different cell designs).
- It is unclear where the Ce goes, whether it is found in the fuel cell outlet water, and what the mechanism is for its loss. Presumably, a better understanding might lead to mitigation strategies. The effect of the cool stack in comparison to an anode purge (slide 11) is unclear. There is a large amount of material generated by this team. It would be quite helpful to clearly map the material between the milestones (slide 7) and the material presented (proper labeling, etc.). This extends to other developments that may not be captured by the milestones.

- The accomplishments toward Ce transport and electrode cracks do not go beyond current literature and patent disclosures. These issues will certainly be resolved by manufacturing engineers in a commercial product. It is unclear how a milestone can be "Complete, continuing."

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- The team has good collaboration with different national laboratories and industries for this project. All of the different institutions have appropriate technical collaborations and interaction on the project.
- The content in the presentation shows excellent team efforts toward achieving the project goals.
- Collaboration partners are well aligned with project objectives.
- Collaborations with other organizations are generally good. The modeling work from Argonne National Laboratory (ANL) on performance and hydrogen crossover has too many critical electrochemical parameters that are variable and used as fitting parameters. For all models, the value of the exchange current density, Tafel slope, and ORR reaction order should be clearly stated and compared to the literature to verify accuracy.
- Collaboration, especially with the other national laboratories and universities, is a strength of this project. One major recommendation is that the researchers should solicit more input from OEMs besides Ballard (especially automotive) to help ensure that they focus on the most critical problems and avoid studying durability issues that have already been solved by industry.
- The project has many team members providing input that seems well aligned; the effort is coordinated and managed well, but it is not entirely clear how much true collaboration is occurring among the partners.
- The project is desperately in need of an automotive OEM collaborator. While it is true that Ballard has past automotive experience and has resumed some automotive work with Volkswagen, Ballard would not be expected to have the same perspective as an automaker that has had a consistent and continuous effort from the stack level to the vehicle level over the past decade. The addition of this collaboration is necessary so the investigators will avoid overlapping work and focus on the aspects of stack failure modes that are in need of more fundamental study. Collaborations with other national laboratories appear to deliver the needed microscopy results, as well as other characterization. Collaboration with the University of Nancy has yielded a segmented half-cell potential technique that was noted at last year's review for delivering results that confirmed the hypothesis about SD/SU degradation mechanisms.
- This project poorly integrates input from the key stakeholders. This list of collaborators seems to be heavily weighted toward national laboratories. If a group attempting to make a profit on a fuel cell system indicates that an area of research is of little value, serious considerations should be given.
- It seems like the researchers are fighting yesterday's battles. Close work with an OEM would greatly aid this effort.
- There are extensive collaborations with varied institutions. LANL leverages a similar European-based project, partly leads the activities of the durability working group, and conducts joint accelerated stress tests with a project tasked to develop accelerated stress test protocols (FC-016).

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.1** for its relevance/potential impact.

- The project is relevant to the objectives of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan. The activities are aligned with DOE's goals. This project is clearly focused on defining MEA degradation mechanisms through experimentation and modeling, and thereby on developing mitigation strategies. Due to the difference in membrane and catalyst composition and quality from various vendors, it is important to understand the similarities and differences in degradation behaviors under fuel cell conditions.
- Improved understanding of component-level effects and mechanisms affecting reliability is valuable. The team needs connections to OEMs or system integrators that have enough long-term data to guide the focus;

carbon corrosion has been studied many times. A rigorous failure mode and effects analysis (FMEA) based on real long-term data is needed to ensure relevance.
- The project aims to explore degradation mechanisms, find mitigation methods, and develop durability models at the component level, including component interfaces and component interactions. Its outcome would help develop durable fuel cells with better knowledge in materials selection and cell design.
- Durable unit fuel cells are essential for successful commercialization.
- Durability is one of the two barriers to the commercialization of fuel cells—both automotive and stationary. This project is relevant to meeting targets. Despite an approach that overlaps with what stack or automotive OEMs already do, this project does show the potential for digging deep into understanding the fundamentals of degradation mechanisms. With the right collaborations; the right cell testing fixtures; the right material sets; and, more importantly, a focus on answering deeper questions, this project could yield the answers that OEMs need. For example, OEMs already understand some of the basics about carbon corrosion, which includes an understanding of how carbon loss, thickness loss, electrochemical area loss, and performance loss are related, and how they are related for different carbons and for different Pt weight percentages. It would be more interesting for this project to understand how the ionomer is affected under SD/SU in terms of a chemical degradation mechanism, or what reactions are involved. LANL has a wealth of chemical characterization tools at its disposal; these techniques should be used so that LANL is not left just relating cell performance and diagnostics to observations from microscopy and energy-dispersive X-ray techniques.
- Many of the phenomena observed in this project are known by the OEMs (e.g., lower Pt weight loading proves more effective than diluent) or conflict with at least some OEMs’ observations (e.g., gas diffusion layer degradation, Ce wash out). Effective SD/SU mitigation control strategies are also well known among many OEMs. It would be more relevant if LANL could develop degradation models that OEMs can use to project the degradation of best-in-class materials as a function of operating strategy.
- The use of a drive cycle is definitely a good idea and of practical value. It is unclear how useful these results are to the automotive fuel cell industry; the trends are well known but for different catalysts and different systems. Issues such as SD/SU are specific to the flow fields used; flow rates; and many other system factors such as the RH of the purge gas, compressor cooling, etc.
- The history of PEMFCs has been one of moving targets, changing materials, and changing assumptions toward operating conditions and balance of plant. If a project is going to be funded for five years, it has to be given the flexibility to move with these changes. Working toward targets established six years ago in a proposal limits the usefulness of this talented group.
- Several components of this work are not considered to be very important by the U.S. DRIVE Partnership’s Fuel Cell Tech Team/OEMs/suppliers.

Question 5: Proposed future work

This project was rated **2.8** for its proposed future work.

- Focusing on the catalyst-layer morphology effect and carbon/ionomer/catalyst interaction (particularly for low-Pt-loaded MEAs) is consistent with the need to reduce cost for fuel cell vehicle commercialization.
- Of all the suggested future work, the effect of the Nafion® ionomer on catalyst durability is of the highest importance and value.
- The future work described is aligned with the proposed work of the project. The team should consider working with Ce-containing electrodes and a Nafion®-XL membrane to better understand the Ce migration behavior. In addition, LANL should expand the use of MEAs to non-Nafion®-type ionomers.
- The following should be removed: conventional carbon corrosion studies (OEM overlap); SD/SU (too system- and cell design-dependent, unless done with OEM); Ce additive work (insofar as it overlaps with what General Motors [GM] has already published); and membrane durability work based on membranes of a generation prior to ca. 2010/2011. The following should be kept: study of catalyst-layer cracks and their effect on membranes, and all catalyst/ionomer interaction and ionomer mapping work (with a focus on developing tools for doing so, and on fundamental understanding of Pt/ionomer or C/ionomer interactions). Pt alloy work should only proceed if state-of-the-art alloys are to be used. Conventional Pt alloys from even 3–4 years ago are considerably different from what has been developed. There should be collaboration with either the GM dealloyed PtNi project or the ANL PtNi nanoframe project. There may also be other supplier

materials that have very recently been developed. These comments apply as well to the section regarding "Fuel cell catalyst widening materials models." Mitigation work needs to follow the development of a mechanistic understanding of failure modes. For example, understanding how to mitigate ionomer poisoning of Pt would follow understanding whether and to what extent ionomer poisons Pt.

- A few topics proposed for future work include defining the effect of individual degradation mechanisms on durability. Post-mortem characterization of long-term—on the order of 1,000 hours or more—test fixtures should be done to set priorities. The team should move on to more applications. It should design mitigation strategies, design accelerated tests, or extrapolate lifetimes more effectively.
- More work needs to be done on Ce, which appears to be in all future PEM systems. We do not have a very good idea of what affects reaction rates, what are competing reaction rates with ionomer degradation, how much is needed, how it competes with Fe, how the Ce:Fe ratio affects degradation, the temperature dependence of the kinetic rates, how Ce leaves the membrane, why it moves to the catalysts layers, etc. The proposed future work is very ambitious for a project that is winding down.
- With the exception of "Discern carbon/Nafion®/catalyst interactions and structure on durability," which should become a primary focus of this project, and "Expand our previously developed models on Pt dissolution," most of the proposed future work will not be valuable to OEMs. Membrane degradation work is only valuable if done on the best available robust materials (beyond Nafion® XL). OEMs know they must eliminate electrode cracks to prevent membrane degradation. OEMs and PEM suppliers have done extensive work on optimizing the form of Ce to prevent degradation and minimize performance loss, and they have developed their own effective start-stop strategies. The team should bring back the plate work because it is known that there is a strong correlation between plate corrosion and membrane degradation. It would be interesting to determine which is the initiator—Fe from the plate initiating PEM degradation or F- from the PEM causing plate corrosion.
- Larger focus should be placed on incorporation of state-of-the art materials (e.g., core-shell and dealloyed Pt alloy cathodes at target loadings), rather than on Pt on carbon, which is clearly unable to meet performance, cost, and durability targets. The team should deemphasize catalyst-layer morphology studies unless results are to be incorporated into a predictive model.
- It is difficult to discern an overall direction(s) and where efforts should concentrate. It is unclear whether the team regularly obtains feedback from OEMs, including for stationary applications.
- The team should keep the focus on the reaction surface.

Project strengths:

- The team is well organized and has the best technical people for conducting the durability study. The team is composed of respectable research organizations with adequate expertise. Overall, the team is equipped with the knowledge base, resources, and industry/academia/national laboratory mix required for the success of this project.
- Collaborations with national laboratories yield characterization results. Investigators have a deep background on fuel cells (>20 years). Despite the overlap with OEM work, most analysis on carbon corrosion is accurate. The project's future direction to look at catalyst/ionomer interactions and to do ionomer mapping is correct.
- This project has access to outstanding analytical and modeling resources through ANL, LBNL, Oak Ridge National Laboratory, CEA, the National Institute of Standards and Technology, and the University of Nancy, which have supported the team's durability studies.
- The project is focused on characterizing and improving the durability of PEMFC components and MEAs, meaning that it is directly aligned with a key DOE barrier. Collaborations are appropriate toward addressing project objectives.
- The project features a well-connected, varied, and experienced team that has access and use of state-of-the-art characterization equipment.
- The results are a robust extension of the previous work, and the principal investigators are knowledgeable of most of the work done in the area. Collaborations are good and effective.
- The project team has the expertise for characterization and developing mechanisms for degradation.
- The project features strong coordination among many national laboratories with various areas of expertise.
- The project team's characterization ability is a strength. The team has widespread capabilities.
- The project features a knowledgeable team with state-of-the-art characterization and modeling resources.

Project weaknesses:

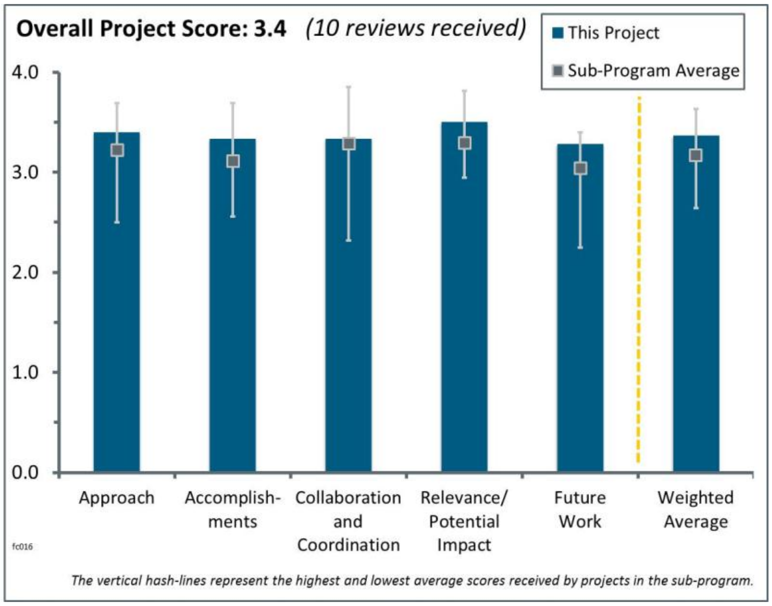
- Much is said about the lack of cooperation with an automobile manufacturer; without a direct contract, the project investigators should work very hard to reach out to OEMs to make sure that their work remains relevant. If OEMs do not want to cooperate or do not think the investigations are valuable, it raises the question of funding this type of work in the first place.
- There is a lack of input from automotive OEMs on the most relevant durability challenges. This project is heavy on diagnostics (which is good), but it would benefit from more parametric studies and designed experiments to understand the impact of operating conditions on the various degradation mechanisms being studied.
- Existing diagnostics such as ECA and EIS have not been applied to their fullest extent to obtain useful information. Some of the results presented have been well established for the last decade and do not provide any new insights. Practical mitigation techniques for SD/SU from easily available patent literature have been ignored.
- A significant portion of the work overlaps with OEM activities. A deeper fundamental probe of failure mechanisms is needed. There is a lack of access to state-of-the-art materials, cell designs, and system operating conditions. There is also a lack of automotive OEM collaboration.
- The project features a combination of a large number of research organizations, which may be a management challenge for the prime organization.
- There is insufficient focus on state-of-the-art materials, and too much focus on characterizing degradation-induced electrode/electrocatalyst changes of previously studied, unstable cathode catalysts.
- More input is needed from industrial partners to prioritize the tasks and phenomena.
- Prioritization of resources and adaptability are weaknesses of this project.
- Mass transport losses seem to be ignored, but perhaps they are not as important anymore.

Recommendations for additions/deletions to project scope:

- The following should be removed: conventional carbon corrosion studies (OEM overlap); SD/SU (too system- and cell design- dependent, unless done with OEM); Ce additive work (insofar as it overlaps with what General Motors [GM] has already published); and membrane durability work based on membranes of a generation prior to ca. 2010/2011. The following should be kept: study of catalyst-layer cracks and their effect on membranes, and all catalyst/ionomer interaction and ionomer mapping work (with a focus on developing tools for doing so, and on fundamental understanding of Pt/ionomer or C/ionomer interactions). Pt alloy work should only proceed if state-of-the-art alloys are to be used. Conventional Pt alloys from even 3–4 years ago are considerably different from what has been developed. There should be collaboration with either the GM dealloyed PtNi project or the ANL PtNi nanoframe project. There may also be other supplier materials that have very recently been developed. These comments apply as well to the section regarding "Fuel cell catalyst widening materials models." Mitigation work needs to follow the development of a mechanistic understanding of failure modes. For example, understanding how to mitigate ionomer poisoning of Pt would follow understanding whether and to what extent ionomer poisons Pt.
- The team should not include the impact of catalyst-layer cracks on membrane durability. OEMs already know they need to eliminate electrode cracks, and they know how to do it. There is fruitful work to be done on bipolar plate durability studies, especially if LANL can get access to plates made from lower-grade metals such as ferritics, which will be lower cost but may be more susceptible to corrosion.
- More emphasis is needed on quantitative analysis to better understand the observed degradation causes and mitigation effects.
- The effect of Nafion® ionomer on the catalyst durability is of the highest importance and value, and it is recommended to be the main focus of future work.
- A joint publication with an OEM regarding the SU/SD work might open the lines of communication and close some gaps.

Project # FC-016: Accelerated Testing Validation

Rangachary Mukundan; Los Alamos National Laboratory



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Brief Summary of Project:

The objectives of this project are to define the correlation of component lifetimes measured in an accelerated stress test (AST) to real-world behavior of that component; validate existing ASTs for catalyst layers and membranes; and develop new ASTs for gas diffusion layers (GDLs), bipolar plates, and interfaces. The project also strives to develop accelerated testing protocols to enable projection of durability and to allow for timely iterations and improvements in the technology.

Question 1: Approach to performing the work

This project was rated **3.4** for its approach.

- The project addresses durability, a key barrier to fuel cell commercialization. The use of available bus durability data was beneficial and provided useful information, even though it is not directly related to automotive work. It was a good use of available resources, because similar data for automotive durability is not available publicly. The project has included the U.S. DRIVE Partnership drive cycle in the analysis, so comparisons can be made between ASTs and what is representative of real-world usage.
- The project has a well-defined approach that is meeting targets. Correlating ASTs with real data is essential to bring research costs down.
- A lot of work has been performed with very many results. ASTs taking the cells up to 1.5 V are questionable because this is beyond the OCV.
- The project features a sound and flexible approach with field-tested materials, some virgin materials, and other materials for ASTs.
- It is very useful to have AST protocols to help fuel cell component suppliers develop more durable products, as well as to help separate different decay mechanisms with these controlled conditions.
- The project features a logical approach that is showing good results.
- Running component-specific ASTs and characterizing the tested samples is tedious but necessary to find the statistical correlations for lifetime projection. The reliability of the obtained correlations requires a sufficiently large amount of the field data.
- The project features a good use of existing data from real operation to formulate test protocols. However, the project’s over focus on GDL degradation may not pay off because it is not observed anymore on state-of-the-art materials.
- It is generally difficult to explain the correlation between materials tests and field tests. However, LANL carefully picked the materials set to show the correlation. It was good to show the differences in degradation rate by AST protocols. The important thing is to understand the AST’s impact on degradation or failure.
- The wealth of data is great.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- The team has achieved excellent detail and accomplishments over the last year. Analyzing ASTs to determine what is too aggressive and what is too passive based on real data is an important step. Defining gaps in ASTs and working to develop ASTs to fill those gaps is also a great accomplishment.
- LANL showed excellent data of degradation and failures with respect to AST protocols (e.g., new and old carbon corrosion ASTs with potential cycles versus potentiostatic, respectively). It is good to distinguish the membrane stress factors of relative humidity cycles and potentials.
- LANL showed good progress in demonstrating the ASTs. LANL should focus on developing relevant test protocols and not on the degradation mechanism for a specific material set, because this differs among material sets. The project has addressed the reviewers' comments very well.
- The team has made good progress over the past year, especially with respect to recommendations on alternate ASTs that should provide higher acceleration factors, which is important because more robust components and materials are being developed.
- A considerable amount of useful data has been collected and analyzed.
- The project has quantified carbon corrosion/oxidation during AST testing and has provided data to show how catalyst layers densify during aging. The carbon support corrosion work has been very beneficial. LANL has identified GDL aging modes. The membrane modeling effort looking at the growth of pinholes appears to be new. This work could be really useful when a pinhole initiation model is incorporated. It is not yet clear how the GDL degradation affects performance. More work should be done to determine how the GDL aging affects performance. It is not clear how much of the membrane degradation work covers new ground versus going over ground that has been previously covered by others. Previous work in the literature has indicated that a combined mechanical-chemical cycle is needed to simulate real-world degradation, and DuPont and others have correlated degradation under combined cycles to real-world degradation. While the ASTs have shown their value in comparing materials and demonstrated that the degradation mechanisms are similar to those in real-world use, it is not clear whether the mathematical correlations that allow one to determine real-world (or U.S. DRIVE drive cycle) durability from AST performance have been developed for most of the tests.
- The project has built up a large set of data under various AST protocols. The statistical correlations for the tested fuel cell components are not explicitly described.
- Metal bipolar plate and interface ASTs do not appear to have been addressed. However, it was mentioned that these activities were previously deemphasized. On slide 9, it appears that the carbon corrosion rate data supports the hypothesis that as corrosion proceeds, the first layer of carbon, which is more corrosion resistant, disappears first, followed by more easily corroded carbon (greater corrosion current), which has a more exposed area (corrosion lasts longer). On slide 13, it is unclear whether the lateral membrane damage is the same as delamination. It is unclear whether the mechanism associated with mass transport losses in the GDL is clear. It is unclear whether changes in carbon surface groups or accumulation of contaminants on the surface affecting porosity or surface properties, etc. have been considered as possible causes. Therefore, perhaps it is premature to claim a good correlation (slide 22). Correlations between accelerated and field data for specific metrics are presented (reviewer-only slides), although the GDL degradation seems to have been left out of the analysis. It is unclear if there is any particular reason why the analysis was not completed.
- It is pretty unclear how the results relate to the "real world."

Question 3: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- Excellent collaboration is evident between Los Alamos National Laboratory, Oak Ridge National Laboratory, and Lawrence Berkeley National Laboratory. Collaboration is evident with other degradation projects funded by the Fuel Cell Technologies Office through the Durability Working Group.
- Excellent team efforts can be seen from the testing data and analytical results given in the presentation.

- LANL has worked with a variety of collaborators and is responsive to recommendations, including those from the U.S. DRIVE Fuel Cell Technical Team (FCTT).
- The project features good collaboration with materials suppliers.
- Collaboration is satisfactory, but it would have been interesting to see other fuel cell manufacturers involved. It is unclear whether Ballard is representative of the industry. The reviewer acknowledges that much of the information is proprietary and other manufacturers may not want to participate.
- The project is well connected with multiple DOE laboratories and industry partners. Additional free support and participation in the Durability Working Group help to strengthen the project.
- The team is varied with extensive experience. However, it would be desirable to gain the support of other industry representatives with additional field data for AST validation.
- Collaboration appears to be limited to ionomer suppliers. This may be because degradation mechanisms are specific to material sets and involve so much know-how that most original equipment manufacturers (OEMs) are not willing to collaborate with their best materials. The project should focus on developing accelerated test protocols that are relevant to real operating conditions. There should be more conversation between European- and Japanese-funded projects as well.
- More interaction with manufacturers/operators is strongly recommended.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- This project is highly relevant to meeting DOE goals. Cheap, quick, and effective ASTs can help manufacturers decrease the time required to assess new ideas and materials, thus helping the industry and DOE meet their targets.
- The project is relevant and addresses durability, a key barrier to fuel cell deployment. While the automotive OEMs may have their own correlations between the ASTs and real-world behavior, that knowledge is not public. It is important for DOE to have correlations between accelerated tests and real-world behavior (or as close to it as it can get with a drive cycle) to be able to understand how the durability of current technologies determined in ASTs compares to the durability needed in real-world usage, and to determine if the ASTs are applicable to the new materials being developed (i.e., accelerate the degradation modes being observed in real-world usage).
- Durability is one of the most significant gaps for automotive fuel cells. Study and basic understanding of degradation and failure modes are important. ASTs should be based on these understandings.
- Durability is a major barrier, and this project was very beneficial to the community’s understanding.
- Development of relevant ASTs is very important to accelerate the learning cycle on durability.
- In view of the recent developments in components durability, ASTs have gained increased relevance.
- ASTs are very effective tools.
- ASTs are necessary to reduce the development time of durable fuel cell components. The impact of the developed AST protocols will depend on the confidence level of the obtained statistical correlations.
- The real impact of the work on fuel cell development is missing.

Question 5: Proposed future work

This project was rated **3.3** for its proposed future work.

- The project is scheduled to end this year; however, future work (presumably for a follow-on project) is described. The proposed future work will expand to include more relevant materials such as Pt-Ni alloy catalysts. The continuation of long-term drive cycle testing is beneficial. Correlation to drive cycle testing will be the next best thing to correlation with automotive usage, but data will be much more available. The evaluation of more accelerated ASTs will be beneficial. New, advanced materials degrade slower, and more aggressive ASTs are needed to determine when they fail.
- There is well-defined future work that will enhance the overall project.
- The proposed future work features a good roadmap to achieving the objectives.

- The reviewer wonders if it would be realistic to consider modeling the combined chemical and mechanical membrane degradation, which would not be trivial, to validate and subsequently use to predict operating conditions that would accelerate the AST. For instance, adding a solvent in the reactant stream would magnify the swelling of the membrane (hydrophobic rather than hydrophilic domain) and could lead to higher stresses (it is unclear if it is relatively easy to implement). Cell operation, rather than OCV, in the presence of an organic contaminant leads to significantly larger amounts of peroxide (without harming the membrane directly).
- The researchers should consider a membrane AST that cycles the current density (at constant inlet RH) instead of cycling the RH, which is more challenging; this will also provide both mechanical and chemical stress, but it will be easier to implement.
- Expanding into membrane electrode assemblies (MEAs) with low-Pt-loaded Pt-alloy catalysts makes the project more relevant to fuel cell electric vehicle (FCEV) product development in the automotive industry.
- The most important objective is to understand the degradation and failure mode mechanism and stress factors rather than evaluating (or selecting) AST protocols. It is still questionable to test with the Fuel Cell Commercialisation Conference of Japan protocols. LANL needs to identify what stress factors are apparent from these tests.
- The focus should be on a precompetitive material set because degradation mechanisms are specific to material sets. To be relevant to real operation, LANL should be focusing on increasing the frequency of stress, not on the magnitude of stress.
- The proposed future work will lead to further results; it is not clear if the impact will be improved.

Project strengths:

- LANL is making good recommendations on advanced AST protocols, which are required. It makes a recommendation on new ASTs based on real-world data, not just FCTT feedback (e.g., GDL AST recommendation).
- LANL is well connected and has a strong project focus. Defining and evaluating ASTs is an area of strength.
- The project features a good mix of accelerated tests and materials characterization to try to get a bit more information on degradation modes and mechanisms.
- The project features a varied and experienced team with good characterization capabilities. ASTs are needed in view of the recently improved materials. LANL has a good approach.
- Strengths include the effective collaboration among national laboratories (for testing and characterization) and industrial partners (for fuel cell components and field data).
- The project features good capture and analysis of the data.
- The established testing capability is consistent with FCTT test protocols.
- The project features open collaboration and good testing capability.

Project weaknesses:

- The unavailability of automotive field data from OEMs is a weakness. If this data were available, this work would be much more useful.
- Several causes could be ascribed to GDL degradation. However, the real cause(s) has not been clearly ascertained.
- It is pretty unclear how the results relate to the “real world” (i.e., support development and improvement). No correlation is seen between the results and measures to be taken.
- There is insufficient FCEV data for developing reliable statistical correlations.

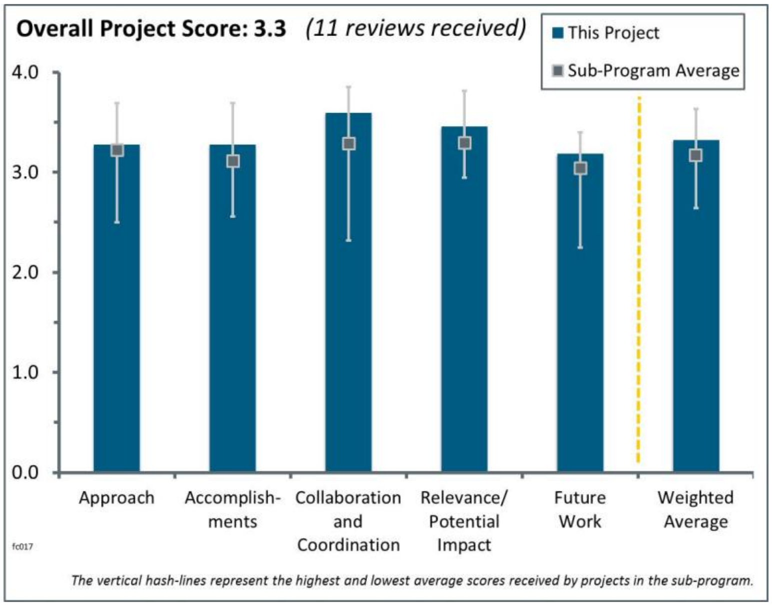
Recommendations for additions/deletions to project scope:

- The project could include catalyst-layer morphology in characterization, particularly for low-Pt-loaded MEAs. The information on catalyst-layer morphology change (e.g., agglomeration) will greatly help voltage loss breakdown by proper catalyst-layer modeling.
- More interaction with manufacturers/operators is strongly recommended. Results have to transform into actions to be taken to improve durability under real conditions.

- It is unclear if there was a requirement to offer solutions to enhancing the durability and performance of the materials, but it would be useful to have ideas presented.
- The team should focus more on studying and understanding degradation and failure mode mechanisms with specific stress factors. It should analyze stress factors in AST protocols to correlate degradation and failure mode, rather than just test AST protocols.
- LANL should find ways to document learnings. There should be more conversation with European-and Japanese-funded projects.
- Work to date has focused on materials that do not meet DOE targets. Future work needs to be done with advanced materials to determine if the degradation modes and acceleration factors remain the same. It would be useful to obtain field data from other applications (e.g., stationary, backup power, and materials handling) and do similar comparisons to determine how aging from the ASTs compares to aging in these nonautomotive applications. Stationary power would be particularly interesting because the lifetime requirements are so long that real-world durability tests in the laboratory are not practical.
- Additional collaborations and field data from industry are recommended.

Project # FC-017: Fuel Cells Systems Analysis

Rajesh Ahluwalia; Argonne National Laboratory



Brief Summary of Project:

The primary focus of this project is to develop a validated system model and use it to assess the design-point, part-load, and dynamic performance of automotive and stationary fuel cell systems. The model will support the U.S. Department of Energy (DOE) in setting technical targets and directing component development, establish metrics for gauging the progress of research and development projects, and provide data and specifications to DOE projects on high-volume manufacturing cost estimations.

Question 1: Approach to performing the work

This project was rated **3.3** for its approach.

- The general objective of the project is of great interest for helping system designers propose an adapted fuel cell system from both technical and economical point of views, and the proposed approach is in accordance with the objective.
- Identifying operational constraints of the fuel cells with regard to pressure and temperature and the impacts on cost requires the sharp focus seen in this project.
- The system modeling approach is sound. The team has responded to input from the industry and added a heat rejection constraint on the stack/system models.
- The approach based on modeling and validation is logical and appropriate for this project.
- Overall, the approach is good and in line in addressing targets that are the focus of the DOE Hydrogen and Fuel Cell Program (the Program). On a high level, the approach of developing a model that is a versatile design and analysis tool, validating the model with data from inside and outside of Argonne National Laboratory (ANL), and applying the model to the issues of current interest is consistent with accomplishing the objectives set out in the presentation. However, the approach that is used in the inner details of the model is important to assessing the potential success of the project. It would be useful to consider including supplemental slides that describe the inputs needed for the system model, the process by which it is calibrated/fitted, and the manner by which certain aspects such as stack thermal capacitance/liquid water/phase change are handled, because they may impact the analysis. These inputs may be appropriate to include in the review slides.
- The approach uses publicly disclosed materials considered to be state of the art. The principal investigator (PI) needs to make some assumptions about the compatibility of these materials in a complete system (even though it may not be completely proven or validated). The model and approach are becoming more realistic and in line with industry expectations every year. The PI works well with industry and ANL's modeling teams to ensure the model is as accurate as possible with the given information.
- This project is well designed to continually identify barriers and set targets by applying the system-level model, based on validated cell and stack submodels, to parametric and trade-off studies. Further validation against actual stacks is desirable, as opposed to the current strategy of extracting effective kinetics on 50 cm^2 cells.
- The project should analyze fuel cell system architecture itself. Currently, some original equipment manufacturers (OEMs) are trying commercialize their fuel cell vehicles; however, their system architectures are varied. For instance, one OEM applied non-external humidification to reduce the cost; this

approach seems to be quite different from the ANL assumption. The project should cover system architecture analysis; for example, it could try to determine the proper system architecture of non-ionomer catalyst-layer membrane electrode assemblies (MEAs) that are sensitive to relative humidity (RH) vs. RH-insensitive MEAs, non-humidification and dry-out mitigation strategies, etc.

- Because this is a multiyear project, it would be good to show a spider-type plot of what is covered, what has been covered in previous years, what has high versus low confidence, etc. (e.g., low temperature, freezing operation, temperature extremes). It would be helpful to establish metrics for gauging progress or orienting reviewers.
- The function of this project is important in terms of guideline and direction making. The approach is good. The impact of newly developed materials on the system is well studied; however, there is still room for improvement.
- The approach and goals are well organized and carefully adapted to the needs of fuel cell researchers and developers. Going forward, more emphasis on end-of-life (EOL) parameters should be integrated.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- The PI has been consistently upgrading this model for many years. The model is updated as new materials and better overall system modeling tools emerge. The U.S. DRIVE Partnership’s Fuel Cell Technical Team (FCTT) and laboratories have worked with the PI to continually improve the model to reflect more realistic systems.
- ANL had updated the model results and compared the impact of the new heat rejection constraint on the overall system cost and showed that the new constraint does not add cost at higher pressure.
- Excellent progress has been made, especially in the area of stack heat rejection.
- The project features a good study of the new fuel cell design requirement ($Q/\Delta T$).
- ANL has updated cell model kinetics to address emerging and maturing designs as well as applied a system-level model to identify cost and operational trade-offs.
- ANL has demonstrated a significant amount of work looking at a number of material configurations that are relevant to next-generation catalysts, heat rejection constraints, and optimization studies related to the system cost/catalyst metal loadings. These are all high-impact areas for fuel cell manufacturers, and a validated system model that provides guidance for optimization in these areas is highly valuable. One issue frequently faced by fuel cell manufacturers is the degree to which variability in a component or operating condition will alter the cost analysis/performance of the fuel cell system. In slide 6, the model does not quite capture the behavior of limiting current for the higher system pressures and higher temperatures. In addition, the plot of mass transfer overpotentials is under-predicted in the low-current-density region, and a similar type of variation across the current density range can also be seen in slide 15. For the system model to accurately predict cost trade-off/system optimization, it would appear to be important to assess the effect of variability in the input data for various components of the system model, in part assessing the type of tolerances that need to be in place from a manufacturer’s standpoint, but also providing an understanding of the precision to which the model can assess differences between materials.
- It seems like there has been significant progress in the development of the tool, and new results have been presented. The work on Pt-loading optimization is very interesting, even if the variable parameters used are not clearly detailed. From a general point of view, critical points for model validation should be better detailed, in particular those dealing with mass transfer. Regarding the compressor, it is unfortunate that only one compressor model is studied. Including a turbo compressor could be interesting. A cost study should be completed that also considers EOL performance. A degradation study was again mentioned but not presented—it is unclear how it will be integrated. Namely, it is unclear how the thermal design will be affected when stack EOL performance is taken into account.
- The project deserves an excellent evaluation regarding the RH and the impacts on the system performance.
- So far, the progress is good. However, the researchers can update the assumptions for system architecture and components for further cost reduction.
- The team made strong progress while integrating major changes to the model, but there was no mention of the model’s availability to the general public.

- It is unclear if there is model validation for the Q/ΔT work. It may be there, but it was not completely clear from the talk or slides. PtCoMn/nanostructured thin film (NSTF) has clear reference data cited from 3M. It would be nice to provide some anchor points or reference points for previous operating conditions. The previously assumed operating points are not clear, nor are the changes relative to that point(s). Regarding ORR kinetics and mass transfer, it would be good to highlight key results better; for example, on slide 18, the key result or highlight is unclear—or perhaps the researchers were just building the ingredients for the cell modeling capability for novel catalysts. Perhaps indicating explicitly what problem is being solved on these slides would be helpful. On slide 20, the conclusion/takeaway regarding the Roots air expander is unclear. The reviewer wonders if it was superior idle power.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.6** for its collaboration and coordination.

- The PI works with Strategic Analysis, Inc. (SA) and key laboratories to build the model and provide key feedback to the partners. The PI has worked well with the FCTT to get feedback from the OEMs and implement changes where possible.
- The collaboration is very good because it has been expanded, as recommended by the previous reviews. The coordination of the project also appears to be good.
- The project features excellent collaboration with system integrators, component suppliers (cell and balance of plant [BOP]), and technical working groups.
- The project features an excellent team working on a focus area for the Fuel Cell Technologies Office.
- The researchers are keeping good communication with other DOE funding projects, OEMs, suppliers, and the FCTT.
- The project features strong input from key stakeholders, as well as great teamwork.
- The project is interfaced with numerous other institutions, including component manufacturers, automotive companies, system component developers, other model developers, and the FCTT. Overall, the interaction is excellent and a high point for the project. It would be helpful to illustrate on an early slide what each partner is specifically contributing or using from the project—this would make it easier to assess the overall level of coordination (although slide 21 does assist in providing a general guide).
- The project is well connected; it is good to see that the researchers are using the new Eaton blower data. It is unclear if there is a reason why the Japanese fuel cell stack developers were excluded.
- The project has been conducted with relevant inputs and collaboration with other organizations.
- Each study can provide important results because of good collaboration. However, although there are a lot of collaborators, there does not appear to be an integrator who can balance all of the information, including the more realistic system information.
- The collaborations seem to be well established and cover the main areas on slide 5. An industrial partnership with a company such as Eaton is a welcome development for BOP component modeling. Because BOP can be an underestimated component for fuel cell systems, it would be great to see more of this type of collaboration.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- The impact of system modeling is huge and aligns well with the Program’s research, development, and demonstration objectives. The impact will be even greater when the model is versatile to different components and takes into account degradation of the system with duty cycles.
- This project clearly supports the Program in achieving its goals. The cost data generated clearly helps manufacturers know what barriers that operational changes introduce.
- The potential impact with respect to continuing to help set DOE targets is high. The dissemination of the modeling tools is an important path to even greater impact.

- The project focuses on the cost aspects of the fuel cell system and uses a system engineering approach to understand the impact of stack performance and operating conditions on cost.
- The work has provided a better understanding of the impacts of certain operating parameters on stack performance.
- The results of this project have a big impact on guiding material research and subsystem development.
- This project provides a baseline for DOE-funded cost analysis.
- The model has limited use to OEMs and fuel cell system builders. Most OEMs have more detailed models that suit their particular needs. However, the model is very useful for several reasons:
  - Provides a useful tool to DOE to help establish technical targets and research and development directions.
  - Provides guidance to interested parties (mostly non-OEMs) on what the major costs and technical hurdles are on a system level.
  - Provides a useful tool to assist all U.S. DRIVE Tech Teams to communicate needs and targets.
- The project has the potential to impact the targets for the Program because it is integrating data from various component suppliers, from both within stack and within system perspectives. There is a risk associated with setting the targets without assessing the impact of noise and the quality of the fit for the data used as input, and this should be addressed. The potential impact of the project is increased by several items that are listed for validation, such as the cross-flow module with the M311.05 membrane. However, it would be further beneficial to consider a manner by which a system validation point (or series of validation points) could be included to assess the accuracy of the model predictions for the optimized systems.
- The reviewer wants to know whether GCTool/Autonomie are available or used by other non-ANL groups. The reviewer believes that Autonomie is but is not sure about GCTool or the package of GCTool/Autonomie. Making such a package publicly available or an easy-to-use interface would be valuable for the fuel cell/vehicle modeling community.
- The impact of this model will be improved if it is used to evaluate EOL trade-offs.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The project features well defined and relevant future work. It will be good to see the progress and validated model for hydrogen ejectors.
- The proposed future work addresses the overall direction in which the industry and the Program are heading, namely alternative advanced alloy/de-alloyed catalysts and the importance of setting targets for the system to optimize the overall cost. Given the importance of the latter, more effort should be undertaken to include additional validation points for the predictions that are coming from the model by either assessing existing systems or working closely with a systems manufacturer. Further, the proposed future work should also assess the effect and impact of noise in the input data on the resulting conclusions related to the cost projections and heat rejection effects/constraints.
- The proposed future work is basically good. A more system-oriented study might be needed by a “real” system designer—preferably from an OEM—to indicate the guidelines and direction for material/subsystem development from a system point of view. That can result in a more realistic projection of further cost reduction opportunities. (The accuracy of cost estimation is not that significant, but the assumption of system architecture and the consisting components is important, which affects the direction and guidelines for material/subsystem development in terms of cost structure.)
- The researchers should prioritize current-day large-cost items, BOP components, and alternative MEAs. Less priority should be given to high-volume cost projections. It is unclear if it is justified to focus resources on moving from ~$57/kW to $52/kW, given that the key issue is not how to reduce the high volume number, but how to span the gap from today’s very high costs to more moderate costs and slightly higher volumes.
- The proposed work is in line with the objectives of the project. However, the degradation work was proposed last year; it really has to be done this year because it may impact the system design ($Q\Delta T$) and the associated projected cost. Degradation should not only refer to MEAs, but also to key components such as compressors and humidifiers.

- The de-alloyed catalyst and NSTF catalyst comparison is interesting. The researchers should study system architectures with these catalyst-layer differences. For example, NSTF (non-ionomer-type catalyst layer) is sensitive to RH and there is a constraint for humidification control. The implications for system architecture are worthwhile to study, as are cost reduction opportunities.
- Additional stack-level verification and validation, at least for mature models, should be included because the kinetics are parameterized based on single 50 cm^2 cells.
- Focus is strongly suggested on evaluating the effects of various design points—especially stack heat load—on system durability/degradation.
- "Durability considerations" will improve the value of this tool.
- The proposed future work sounds fine; however, it has not changed since the 2103 DOE Hydrogen and Fuel Cells Program Annual Merit Review. It is unclear how long this is going to remain as "proposed future work." The team needs to prioritize alternate MEAs with advanced alloy catalysts, dealloyed PtNi on NSTF (3M collaboration), and dealloyed PtNi on corrosion-resistant carbon support (ANL catalyst project with Johnson-Matthey Fuel Cells Inc. and United Technologies Research Center as partners).
- The PI will continue to update the model as relevant data and information is provided.

Project strengths:

- There is a high level of collaboration with other institutions. The project addresses the coupling of the system and the stack, which is hugely important to balancing stack design aspects versus system constraints versus total cost. Other strengths include the project's analysis of various catalyst materials, and that it directly discusses the impact of specific design constraints on overall cost and targets for cost.
- The project features a systematic analysis of a fuel cell system, which can be a strong and important guideline for material research and subsystem development. Another strength is the collaboration with various suppliers, which facilitates study of each subsystem/material cost from "realistic" information.
- A detailed modeling framework has been established, and thorough modeling capability and sensitivity analysis has been presented. Developing physical modeling capability for novel catalysts is valuable. Interaction with an industry partner for the BOP component is welcomed.
- The model is continually updated and refined as information becomes available. The PI clearly communicates his assumptions and makes the information readily available to those who are interested.
- It is a very complete model that takes into account many mechanisms involved in the operation of a fuel cell system. The parallel cost estimation with SA is appreciated.
- Project strengths include the validated system model baseline and communication with information sources.
- Strengths of the project include its detailed analysis, and the fact that it is highly focused and connected.
- The project features excellent teamwork and good fundamentals.
- Strengths of this project are its technical approach and collaboration.
- This project has proven to be adaptable and seeks input from a diverse group of stakeholders.

Project weaknesses:

- The assumptions of the analysis may be old, or too stack/MEA/material oriented. Although there are a lot of collaborators, there does not appear to be an integrator who can balance all of the information, including the more realistic system information.
- The following are more presentation critiques rather than project weaknesses: the presenter should highlight key points on slides, provide reference values from previous years, and provide better context for key problems being solved.
- ANL does not consider the impact of variability in input data (such as catalyst characterization). Additional validation of fuel cell system (FCS) outputs for various systems is needed. Another weakness is the lack of specific details related to the approach used to treat different components of the stack/FCS.
- Durability constraints have not been implemented, even though this was mentioned two years ago. Data used for the optimizations rely only on 50 cm^2 single-cell data. Stack validation is lacking.
- The components and subsystems selected may not always be compatible in real life.
- The researchers should consult the FCTT for validated $Q/\Delta T$.

- The lack of progress is an area of weakness.
- The project focuses on too many parameters.

Recommendations for additions/deletions to project scope:

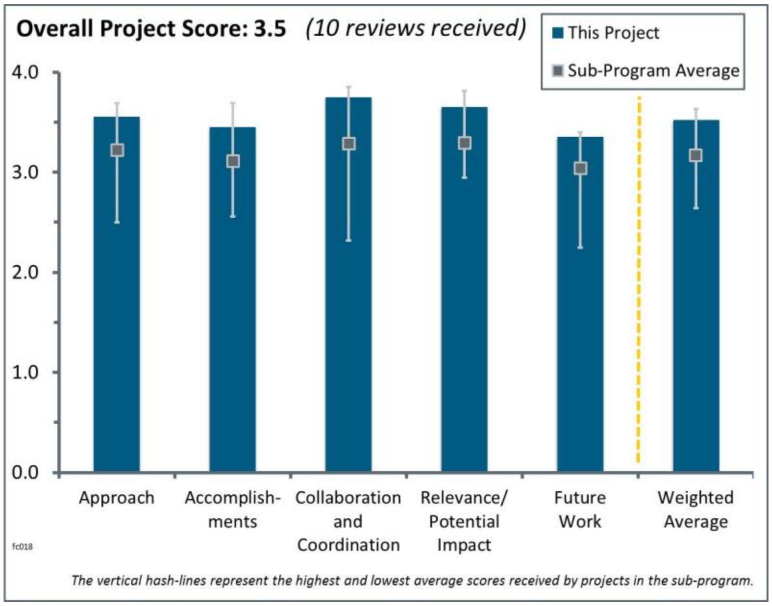
- It would be better to have one person from an OEM serve as the total system integrator. The assumptions of the current analysis may be old or too stack/MEA/material oriented. A more system-oriented study would be better; one that first considers overall system architecture and standard materials. Of course, a material-oriented study is important, but a more systematic study can be done. For example, if air pressure is reduced to around 150 kPa, the system designer will add a blower, not a compressor, to the system to reduce costs. The humidifier can be eliminated if the membrane and/or water management are improved. Therefore, the accuracy of cost estimation is not that significant, but the assumptions for system architecture are important, which affect the direction and guidelines for material/subsystem development in terms of cost structure.
- This year the PI switched to a neural model; perhaps a bit more information could be provided regarding how this change affects the outcome of the model—a bit of a sensitivity analysis of the old versus the new. He did mention that it provides a more realistic result when using data points outside of the empirically available data. The presenter should provide more information next time on where this observation was noticed most or had a key influence in the outcome.
- The project scope should be expanded to cover a system architecture study. The system architecture was not changed for the last 2–3 years, but based on technology advancements, the system architecture itself is also advancing, such as non-external humidification and passive anode recirculation (single stage). MEA technology is also advancing, including the incorporation of non-ionomer catalyst layers into RH-insensitive MEAs. This project is expected to apply technology opportunities from real-world industry as well as DOE funded projects. More information collection and benchmarking are recommended.
- The team should pursue additional validation points for the FCS outputs on a system-/stack-level. They should include, for example, analysis of the effect of experimental variability/component manufacturing variability on the FCS output and predictions for cost.
- ANL needs to consider moving this model to an open-source-code framework. The team needs to collect data in a cell (National Institute of Standards and Technology/General Motors) with coolant ΔT and validate the data against the model.
- The researchers should focus on incorporating degradation parameters and EOL trade-off studies related to stack and system components.
- The model should be validated against stack data.
- The reviewer questions the general motivation of this work—not about the modeling work in and of itself, but rather for DOE management. This work seems to be optimizing costs around the cost target of $50/kW for fuel cell electric vehicles, but today’s challenge is not how and whether the system can be optimized from $50/kW (+/- $10/kW), but how to move from a $70,000–$100,000 vehicle cost with high stack costs and durability and manufacturability issues to a $20,000–30,000 vehicle cost. The way to model durability was brought up and the lack of data was mentioned. It would be good to see more programmatic focus on how to bridge the large-scale cost chasm in real and practical ways (e.g., how to move from >$1,000/kW stacks to $500 to $200/kW), which may include detailed modeling. Modeling the dynamics of optimized fuel cell systems is clearly important, as are the kinetics and mass transport of novel catalyst materials, but the Program should strongly consider cost limiters and pinch points that exist today.

Project # FC-018: Fuel Cell Transportation Cost Analysis

Brian James; Strategic Analysis, Inc.

Brief Summary of Project:

Strategic Analysis, Inc. (SA) updates its cost analysis of automobile and bus fuel cell systems annually and explores alternative subsystem configurations. The cost analysis is used to assess the practicality of proposed power systems, determine key cost drivers, and provide insight for direction of research and development priorities. The project team completed the 2013 Automotive & Bus Power Systems Cost Report and analyzed two new subsystems: the Johnson-Matthey Fuel Cells Inc. (JMFC)-style dispersed PtNi-on-C catalyst and the Eaton-style twin-lobe air compressor-expander.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.6** for its approach.

- The approach has been vetted continually by the U.S. Department of Energy (DOE), the U.S. DRIVE Partnership's Fuel Cell Technical Team, and many individual organizations and companies. Adjustments are made based on feedback.
- This project conducts a thorough cost analysis of automotive and bus fuel cell systems using well-defined component, stack, and balance-of-plant (BOP) cost assumptions at various production volumes. The revised cost analysis using a Pt cost of $1,500/troy ounce is more realistic. The vetting of stack and BOP cost assumptions by industry throughout the project is an important part of the project.
- The project is well designed and well integrated with the systems analysis work at Argonne National Laboratory (ANL).
- The project features a rigorous approach with sharply focused objectives.
- Generally the approach is very good, but more emphasis on alternative systems and technologies would help the community to understand what system options might make the most sense from a cost perspective, and what technology improvements might be most impactful. Some examples would include the following:
    - Low-pressure polymer electrolyte membrane fuel cell (PEMFC) systems (i.e., no air compressor, just an air blower).
    - Transportation systems with different degrees of hybridization and fuel cell sizes (e.g., an 80 kW bus system [or even smaller]).
    - Tornado plots that include the most impactful parameters (i.e., the most expensive components), such as the membrane, which is not included on the plots on slide 34. The membrane is more expensive than all of the other materials listed other than Pt (e.g., more expensive per square meter than the plates, EPTFE, and gas diffusion layers [GDLs]).
- Changing to W. L. Gore & Associates (Gore) membrane electrode assemblies (MEAs) and Pt-Ni-C catalysts improves the believability of these studies. In terms of examining the cost of support Pt, it is unclear if that can be evaluated by looking at cat-convertor technologies.
- The production capacities spacing looks uneven (systems/year). The steps are currently 900% increase, 200%, 167%, 25%, and 400%. The researchers may want to consider something a bit smoother past the 10,000 systems. For example; 30,000; 70,000; 200,000; and 500,000 systems/year. As it stands, the difference between 80,000 and 100,000 systems/year is not as important as the difference between 100,000

and 500,000 systems/year. A twin-lobe compressor is a more adequate choice for the application over centrifugal—it is good to see the update. The reviewer is concerned about back-leak of this compressor style, especially at low flow rates, as well as noise levels. The technology may have come along significantly, but the reviewer's personal experience with compressors from 15 years ago was of low efficiency and extreme noise. The team accomplished great work on the catalyst processing costing. It was unclear if the peak stack temperature is the average temperature of the stack. It was also unclear if the peak stack temperature is the hottest point of a cathode catalyst, and if not, what is.

- This has been a good and consistent continuation of the costing effort.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.5** for its accomplishments and progress.

- Important accomplishments include updating the cost/volume numbers for buses, imposing the Q/ΔT limit, and adding a plate-frame membrane humidifier to BOP.
- The project is accomplishing project goals, and the research team has creatively identified pathways to a greater understanding of the cost of PEMFC systems.
- Incorporating Q/ΔT, Gore MEAs, and carbon-supported catalysts are all good improvements made in fiscal year 2014.
- This was a great update—this type of consistent multiyear analysis is very useful for other DOE Hydrogen and Fuel Cells Program (the Program) technology development guidance.
- The annual update was performed successfully. Changes to inputs were executed as necessary.
- The accomplishments give a good indication of the cost to be expected.
- Although the cost projections went up (bad!), the justifications provided for these increases were valid and reasonable. However, it would have been good to see more progress on alternatives that could also help the cost projections, such as the use of dispersed Pt/C catalyst layers (instead of nanostructured thin film [NSTF]), because these are presumably lower cost, and the evaluation of low-cost molded-carbon-composite bipolar plates.
- The project team continues to do an excellent job in refining and updating the input parameters and assumptions. In regard to the catalyst, an explanation of the benefit of a dealloyed PtNi versus an NSTF PtCoMn system would be helpful. If the PtNi catalyst enables lower Pt loading, it is unclear how this would impact the current Pt loading assumption of 0.153 mg/cm^2 of Pt. There appears to be a significant decrease in the power density from 692 to 641 mW/cm^2. It is not clear why operating at a lower power density would result in a lower system cost.
- The components design and fabrication process for bus application should select those that have low cost at low fabrication volume. Current analysis uses the same process for automobiles and buses; this is not suitable, because their production volumes are different.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.8** for its collaboration and coordination.

- The national laboratories (i.e., ANL and the National Renewable Energy Laboratory) provide crucial support for model input. The collaboration with the different industries (i.e., stack, stack component, and BOP) is crucial in vetting the cost analysis results and assumptions.
- SA collaborates with all types of organizations and stakeholders. SA's excellent integrity and reputation facilitates collaboration.
- Collaborations are good; the way to make them better is to get real input from the automotive original equipment manufacturers (OEMs), which will be difficult to obtain.
- The feedback loops via industry and national laboratory collaboration seem to be well orchestrated.
- The collaboration with many relevant stakeholders (e.g., OEMs and institutes) supports the viability of the results.
- The project has an extended list of collaborators.

- 3M is not listed as a collaborator; hopefully this is an oversight. 3M is a leader in membranes and manufacturing processes for unitized MEAs (i.e., GDL + catalyst coated membrane + seals). 3M also provides NSTF (which is less important because it is not technically viable yet.)

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.7** for its relevance/potential impact.

- This is absolutely critical analysis for the Program, especially at a time when investors would like more eyes on the potential cost of fuel cell electric vehicles—one of the most important factors in market adoption.
- The project is an independent study of fuel cell system costs for the transportation markets. It fully supports the Program objectives.
- SA’s cost model is a bedrock of Fuel Cell Technologies Office (FCTO) program planning, helping to identify high-cost areas.
- The project gives a clear indication of expected cost.
- The project is critical to the Program because it projects the cost for PEMFC systems at a production level consistent with industry demands. The validation of the approach needs to be continually reviewed by DOE to ensure the quality of the price projections.
- This project is required in some form for DOE to understand where investments are required and how to best use its funds. However, the researchers should also evaluate what effect DOE can have in those areas compared to OEMs.
- This project would have much greater impact if certain recommendations were followed. The reviewer would also expect more progress per year than what was delivered this year.

Question 5: Proposed future work

This project was rated **3.4** for its proposed future work.

- The proposed future work is a logical and consistent continuation of work.
- The beauty of this work is its consistency from year to year.
- The “detailed cost analysis” on high-impact BOP components should be compared in terms of high-volume manufacturing and automotive components (e.g., fuel injectors). When looking at the complexity of a fuel injector, it is hard to understand why they are not more expensive.
- Going forward, the team should prioritize validation of the stack model against experimental results and optimizing operating conditions for both car and bus applications, as well as analyzing high-impact BOP components.
- The researchers should proceed with the plan to add a detailed cost study on high-impact BOP components.
- Production quality control should be better defined and updated.
- There seems to be a difference between SA’s cost projections and those developed by others. Future work should address this difference and account for it in terms of different cost definition, assumptions, methodologies, etc.
- BOP has become more important, if not equal, in terms of cost than the fuel cell stack, but it remains the last analysis on the list.

Project strengths:

- This has been a well-executed project that helps evaluate the state of the technology for DOE guidance purposes. It was good to examine the cost based on a more traditional catalyst (i.e., Pt-Ni-C) and Gore MEAs. That provides a more realistic expectation of where the Program stands in terms of automotive fuel cell cost.
- The experience of the analysis team and its ability to access and analyze component and system information are the greatest strengths for this project.

- The project features a comprehensive approach with well-planned feedback from critical industry partners.
- This project has very good collaboration with OEMs and relevant institutes.
- The project carries out very rigorous, detailed, and technically supported calculations.
- This project strives to use a valid model of the systems and also validate costs with industry.
- The project provides a fuel cell cost breakdown and directions for future further cost reduction.
- The strength in this analysis is the collaboration with industry to vet the assumptions and results.
- The project's flexibility and integrity are areas of strength.

Project weaknesses:

- The project does not do enough to make a connection between its cost estimates and the cost of actual fuel cell manufacturers. There is only one comparison made—that of the bus fuel cell projection and a general statement from a fuel cell manufacturer that its estimates are in the same neighborhood. The community would like to see SA's cost estimates extended to lower manufacturing volumes and compared with real-world actual fuel cell prices.
- The costing approach for the bus power systems is mainly a simple expansion of the automotive work; for example, it used the same MEA. It is very unlikely that the MEAs for the two applications will be the same, specifically in terms of membrane and catalyst loading. The hybridization for buses will also be significantly different.
- The project team has spent several years on the cell stack, with only a small portion of its time on BOP and systems. The effort should increase its focus on BOP.
- 3M and JMFC catalyst layers need further validation with respect to stack performance and durability.
- The progress over the past year was not too impressive.
- The researchers did not separate the high-volume automobile and low-volume bus applications analyses.
- There are no detectable weaknesses.

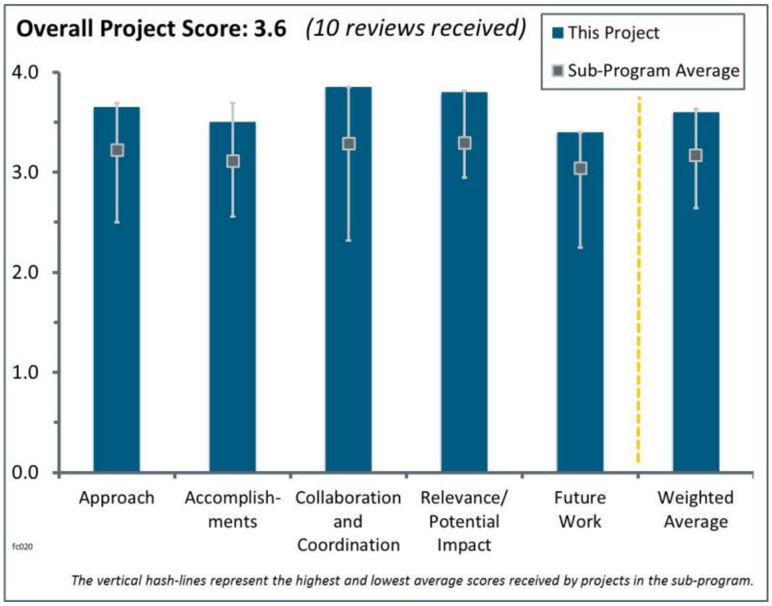
Recommendations for additions/deletions to project scope:

- The project should continue as proposed.
- It is probably time to just leave NSTF out of cost studies related to current cost estimates. The researchers should get guidance on the compressor work from the automotive OEMs in terms of what turbochargers cost. A valuable expansion of this project would be to examine the smaller portable power fuel cell applications, as well as low-temperature stationary fuel cells, to determine if/as those start to be commercialized in the thousands of systems/year range, whether this could increase the speed of fuel cell technology commercialization in the transportation sector.
- The automotive fuel cell cost curve seems to be leveling off at \$40/kW$_{net}$, compared to the target of \$40/kW$_{net}$. A waterfall chart could be instructive in identifying how to get to a lower cost curve.
- Cost analysis should present the trade-off of system versus MEA materials to achieve lifetime durability requirements.
- The project (and the Program) should focus on reporting cost estimates at the 100,000 systems/year level, rather than 500,000, to be consistent across DOE Office of Energy Efficiency and Renewable Energy programs.
- The reviewer wants to know if it is possible to analyze the limit of cost reduction based on foreseeable future technologies.
- The project should reduce emphasis on cathode catalysts and increase emphasis on BOP.

Project # FC-020: Characterization of Fuel Cell Materials

Karren More; Oak Ridge National Laboratory

Brief Summary of Project:



Research objectives for this project are to: (1) identify, develop, and optimize novel high-resolution imaging and compositional/chemical analysis techniques and unique specimen preparation methodologies for the µm-to-Å scale characterization of material constituents comprising fuel cells; (2) understand fundamental relationships between the material constituents within fuel cell membrane electrode assemblies (MEAs) and correlate these data with stability and performance; (3) integrate microstructural characterization within other U.S. Department of Energy (DOE) projects; (4) apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes to elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss; and (5) make capabilities and expertise available to fuel cell researchers outside of Oak Ridge National Laboratory (ORNL).

Question 1: Approach to performing the work

This project was rated **3.7** for its approach.

- This project uses electron microscopy for the characterization of fuel cell materials. It has two main missions: (1) developing methods and procedures in electron microscopy for fundamental studies on fuel cell microstructure and nanostructure (e.g., to better understand mechanisms of material degradation), and (2) to be a resource to the fuel cell research community in applying these methods and procedures in support of other research projects. Normally, a rating for "approach" would be based on which technical means are being employed to answer a given question or achieve a desired result; here, this project is bounded by electron microscopy. However, the tools and the techniques it enables are so clearly essential that it is an outstanding "approach" to have a project focused on advancing such crosscutting metrology capabilities.
- This project develops novel microscopic techniques and methodologies to fundamentally understand nanoscale materials interaction within the MEA—an important aspect in understanding fuel cell performance and degradation. The support provided to other DOE project teams and industry is excellent.
- The work is effectively applying state-of-the-art electron microscopy techniques to the characterization of MEA material constituents from µm-to-Å scale. It is also utilizing advanced analytical and imaging techniques in the evaluation of microstructural and microchemical changes to elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss. This degradation effort is a very important activity.
- The proposed approach is appropriate in the way that it is fully collaborative in nature and aims to benefit the entire fuel cell community in order to have a deep understanding of materials evolution in the MEA components. The project share with 25% for "open research" is also appropriate to allow for the evolution of more instrumental investigations that will be possibly applied to the main projects' issues and, in particular, the materials degradation.
- This ongoing characterization project supports other DOE projects and provides the fuel cell community with access to state-of-the-art microscopic capabilities. Understanding fundamental relationships between

microstructure over the range scales and performance is of the most importance to any progress in the commercialization of fuel cells.

- The investigators continue to listen to their partners and are developing methods that are in line with the critical needs of fuel cell research. This project seems to balance its resources between new method development and supporting requests very well.
- The use of advanced microscopy to examine the MEA, catalyst, and ionomer in the electrode layer will enable the design of new fuel cell components that will have higher performance and durability and lower cost, thereby meeting the three goals of the fuel cell program
- The work has been focused on addressing durability and performance—two key barriers to fuel cell commercialization. The work is integrated well with other efforts. This group provides electron microscopy services and expertise to numerous DOE Fuel Cell Technologies Office (FCTO)-funded projects. The microscopy work at ORNL has been critical to evaluating carbon corrosion and catalyst-layer degradation/densification during aging. Recent work has focused on developing techniques to characterize the ionomer in the catalyst layer, an area about which little is known but may have a large impact on performance and durability.
- Currently, mass transport and durability (retention of high oxygen reduction reaction [ORR] activity) is one of the most important technical focus areas. The project is trying to establish ionomer and catalyst dispersion in the catalyst layer in high-resolution microscopic/spectroscopic approaches.
- This project does not have specific milestones; instead, the focus is to test and analyze new materials as they become available from the project partners.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.5** for its accomplishments and progress.

- This is clearly a productive project, and the presentation was rich with results from the past year. Slide 4 groups various projects into the broad headings of component durability, novel catalysts and supports, and ionomer studies, with much of the presentation given to discussion of the latter (a theme this year in response to reviewer comments from last year). Here, the DOE goals are not system specifications, but rather the metrological goals of being able to provide quantitative diagnostics on the composition, distribution, and degradation of ionomer coatings. This project develops a unique source of information from which rational progress toward the system specifications may be achieved.
- The team has made excellent progress with characterizing the ionomer layer. The practical limitations related to sample preparation should be discussed in the Program's Annual Merit Review forum. The applicability of these methods to degraded materials is critical, and the limitations related to the microscopy methods discussed are an important component toward an evaluation of progress.
- The project accomplished a great deal; imaging soft ionomers in the presence of metal catalyst particles and the initiation of in situ studies are technologically extremely challenging, but these efforts have been accomplished in this project. A great deal of data was collected on relevant catalysts and electrode structures for project partners.
- The project has achieved excellent outcomes for ionomer dispersion analysis with energy dispersive X-ray spectroscopy (EDS) maps to support catalyst-layer study for the enhancement of mass transport and ORR activity.
- The project contributes significantly to a fundamental understanding of the degradation mechanism. Carbon corrosion is utterly important to state-of-the-art fuel cell catalysts. Achievements in in situ electrochemical microscopy will present new, invaluable insight into electrode-layer structure and degradation. The high-resolution EDS capability adds very important chemical information to the transmission electron microscopy's (TEM's) excellent morphological information. The progress in the imaging of ionomers is of great importance. It is not clear whether the conditions for imaging ionomers in TEM (i.e., cooling and low electron doses) will be transferable to in situ electrochemical microscopy.
- Three main points have been pointed out this year:
    - Nafion® characterization by TEM: This is difficult to observe because of Nafion degradation under the beam. Therefore, the operating conditions have been successfully adapted by using electron energy loss spectroscopy (EELS) and EDS. The quantification of the profile obtained at

low electron dosage seems correct even though the proposed interpretation might need to be confirmed due to the level of noise. Mapping at higher electron dosage is nice, but the proposed conclusion about the ionomer instability is not convincing. Actually, because the aging test also degrades carbon, evolution in the ionomer distribution is normal and a conclusion cannot be drawn on its stability.

  - Carbon corrosion analysis: The given conclusions are that agglomerated particles enhance carbon corrosion and a better dispersion is beneficial. These are answers to a recommendation from last year. The presented pictures dealing with agglomerates are not really convincing. The effect of a better Pt distribution on electrochemical surface area (ECSA) seems important, but the associated pictures have not been shown. The reviewer asks if they were confidential. The optimized catalyst on low surface area carbon (LSAC) degrades less during carbon corrosion accelerated stress tests (ASTs), but it is unclear regarding catalyst degradation ASTs involving the Ostwald mechanism.
  - In situ observations: These are the first results presenting catalyst evolution in in situ TEM. Congratulations! The resolution limitation is unclear. It is also unclear whether the observation in a liquid medium would enable study of the ink distribution (solvent effect).
- Researchers have made progress in characterizing ionomers in the catalyst layer. ORNL has developed techniques to minimize sample damage during analysis. The group continues to provide valuable data to the fuel cell community. The in situ electrochemical microscopy has been slow in development and has not yet demonstrated its potential in fuel cell studies.
- The work to understand ionomer damage by the electron beam is very important. It seems that there is still some F loss under LN_2 conditions, so the question arises whether this methodology can be used as a quantitative measure for ionomer degradation. Furthermore, it would be interesting to map out S to understand its location in reference to the Pt particles as well; changes with degradation could give an indication of the local loss in ionic conductivity in the catalyst layer. In regard to the in situ TEM, this reviewer’s understanding is that the electrolyte has to be drained before imaging, so changes in the electrode component composition and structure will not be captured in real time and thus will be difficult to correlate with in situ fuel cell results.
- This project is an ongoing project. The principal investigator (PI) uses in situ microscopy to analyze catalyst dispersion, compacting compression effects in cathode layers, ionomer distribution quantification within the catalyst layer, etc. It is up to the partners to use the information from the results to improve materials and subsystems.
- ORNL completed the parametric study of ionomer thin films with General Motors (GM) and collaboratively published the results. This study establishes baseline conditions to quantitatively assess ionomer structure and composition in an electron microscope.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.9** for its collaboration and coordination.

- This project features excellent, extensive collaborations with the following: Los Alamos National Laboratory; General Motors; 3M; Automotive Fuel Cell Cooperation; Ballard; Nissan Technical Center North America; Ford Motor Company; the University of Tennessee; Argonne National Laboratory; CEA-Grenoble, France; IRD Fuel Cells; Fuel Cell Energy; and McMaster University, Canada.
- Collaborations are numerous and of high quality. It is good to establish new collaborations, even international ones, to provide access to unique imaging/analysis (i.e., microscopy) capabilities in order to more quickly meet the project targets.
- This project is highly collaborative, with service to the fuel cell community being one of its main missions. Slides 2 and 4 list many of the major partnerships.
- This project is a model of excellent international collaboration, due to the work with CEA (France) on EDS map microscopic analysis on ionomer dispersion.
- The approach of the project is to collaborate with industry, academia, and national laboratories on their needs and problems and to make state-of-the-art microscopic capabilities available to collaborators.
- This project features good collaboration with both national laboratories and industry. This group is utilized by many FCTO-funded projects.

- A large number of collaborators from industry, national laboratories, and universities are associated with the project and cover the essential stakeholders.
- The PI collaborates with key original equipment manufacturers (OEMs) and academia. There is no need for more partners to ensure the quality of work/progress, etc. The PI should be open to providing other OEMs with her tools as needed.
- The project features a very comprehensive set of national laboratory and industry collaborators. However, there are no university-led teams, so there may be an issue with imaging next-generation materials that come out of more basic science projects as they become incorporated into the more applied DOE Office of Energy Efficiency and Renewable Energy mission.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.8** for its relevance/potential impact.

- This project is highly relevant for achieving the FCTO Multi-Year Research, Development, and Demonstration Plan (MYRDDP) goals and objectives of better fuel cell performance, greater fuel cell durability, and lower fuel cell costs. On the cost front, microscopy is essential for understanding the behavior of catalysts and how catalyst loading might be reduced. On durability, a central theme of this project is to diagnose and better understand degradation mechanisms at the microscale and nanoscale (i.e., atomic scale). This project is essential to understanding the relationship between materials synthesis, microstructure, and performance.
- Understanding fundamental relationships between microstructure over the range scales and performance is of the utmost importance to any progress in the commercialization of fuel cells, which is directly relevant to the Program’s goals and objectives. The relationship between the structure of electrode layer components, the chemical and morphological changes occurring during fuel cell operation, and its durability is key in advancing durable materials and devices.
- This project is highly relevant to the Program’s goals because it is essential to image catalyst, electrodes, and MEAs at the length scales only accessible to advanced microscopy so that these can be validated and the changes occurring during degradation can be quantified.
- The project aligns well with DOE objectives. It supports a number of DOE projects and industry by looking at the microstructure and nanostructure of MEA components, which is crucial to understanding fuel cell performance and degradation.
- The project aligns well with the Program’s objectives and has the potential to advance progress toward the Program’s goals and objectives. A new technique has been developed for understanding a variety of problems in the areas of MEA synthesis, microstructure, and performance.
- This tool represents ideal collaboration between the national laboratories and industry. This is a good example of a tool that is not available to most industry partners yet still provides valuable insight into material and system performance that will allow the OEMs to improve their designs.
- Microscopy expertise and state-of-the-art capabilities are important to identifying materials degradation mechanisms, which are critical for improving materials structure for enhancing stability and performance. The team did a very good job of communicating the results through numerous paper publications. This increases the impact of the project to the entire fuel cell community.
- This project is critical to understanding fuel cell materials structure and how that structure evolves with usage.
- Relevance: This project remains focused on the needs of fuel cell developers. Impact: The lead time for a partner to get data was not discussed. Short lead times will drastically improve the impact as these new methods become available.

Question 5: Proposed future work

This project was rated **3.4** for its proposed future work.

- The ionomer work on the understanding of ionomer distribution within the catalyst layer and ionomer degradation with aging is important work that needs to be correlated with experimental data from fuel cell testing. It is not clear that the in situ tool will provide the desired insight into structural and compositional changes in the catalyst layer.
- The proposed future work is good and logical. Now that proper imaging and analysis conditions for studying ionomers are in place, the plan is to expand ionomer studies to specifically focus on aging effects as well as electrode/membrane interfaces.
- Continued focus on the ionomer layer is a great plan. Statistical descriptions of ionomer coverage and thickness are highly desired.
- The extension of the work to understand the interaction of the ionomer will be very important and will shed much-needed new light on electrode functionality and degradation. The in situ catalyst studies, if they can be shown to be fuel cell relevant, will be extremely beneficial to catalyst development.
- The project's future work will continue to be motivated by challenges from the U.S. DRIVE Partnership's Fuel Cell Technical Team. The immediate future work, as laid out on slide 24, is appropriate.
- The future work is in line with current progress and deficiencies.
- The proposed future work is appropriate. Because the analysis technique is now mastered, studies on ionomer degradation should go on (e.g., with evolution of ionomer profile and distribution around C). The current studies do not answer the question of how ionomer degrades if it degrades. Catalyst degradation ASTs involving the Ostwald mechanism should complete carbon corrosion ASTs for the optimized catalyst on LSAC.
- It is recommended to implement EDS mapping equipment to establish the capability for ionomer dispersion microscopic analysis domestically.
- The researchers should continue to analyze new materials as they become available.
- A large portion of the future work appears to be focused on ionomer characterization issues, which are a major need for the fuel cell community. The in situ work appears to be aimed at solution work, or rotating disk electrode (RDE)-type conditions, which are quite different than actual fuel cell conditions.

Project strengths:

- Areas of strength include the relevance and high quality of the involved partners developing advanced characterization techniques to better understand degradation mechanisms at the materials level. The consortium is open to new collaborations if suitable for the project and disseminates the achieved results to the fuel cell community.
- The project provides a strong analytical tool to OEMs that otherwise is not available to most industry partners.
- The project's strength is the development of core competency in the area of microscopy and the crucial support to other DOE projects and industry.
- A strength of the project is its ability to use high-resolution microscopic and spectroscopic analysis to support fuel cell research. It has the components and facility to support fuel cell research.
- Strengths of the project include its development of crosscutting metrological techniques and its collaborations.
- The project offers outstanding characterization capabilities and expertise in the fuel cell materials.
- The project features advanced microscopy and a world-leading, state-of-the-art facility.
- The project has good collaborations and provides a valuable service to the fuel cell community.
- The project reacts quickly to the needs of fuel cell researchers.
- ORNL has the capability to accomplish this work.

Project weaknesses:

- This project has no weaknesses.
- No weaknesses have been identified.
- The project team needs to do in situ catalyst testing in the ionomer to be fuel cell relevant; RDE studies are limited to benchmarking because the catalyst in a fuel cell—especially next-generation MEAs operating at drier conditions—will be more influenced by the ionomer, making aqueous electrochemistry less relevant.
- The project is not focused enough on aged MEA in real operating conditions.
- Some measurements and projects rely on facilities found overseas.
- The project relies on foreign capability for ionomer analysis (EDS mapping).
- The capability for ionomer characterization at a high resolution is not available at ORNL.
- The project may lack in-depth focus in some areas with such a broad mandate.

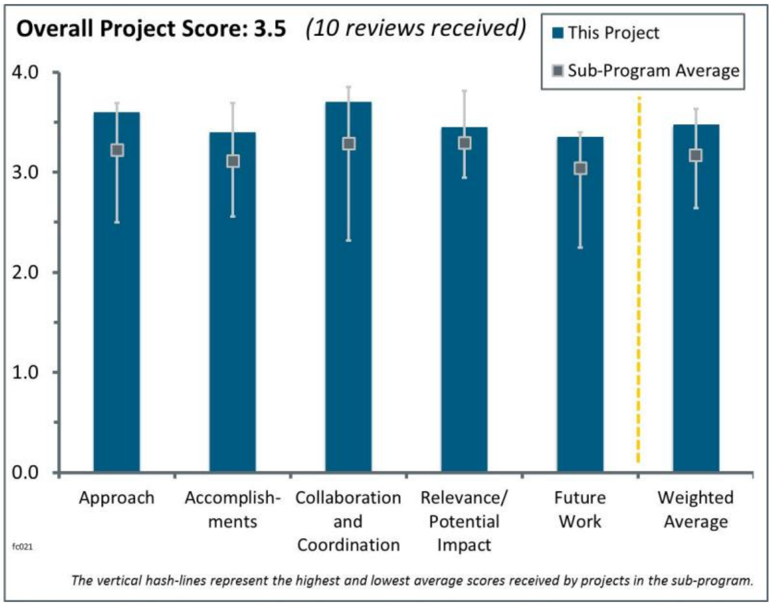
Recommendations for additions/deletions to project scope:

- More of the same would be excellent.
- The researchers should conduct analysis on aged components in real operating conditions, allowing them to validate the mechanisms deduced from ASTs. The team should also conduct analysis on bimetallic catalysts. These could be investigated in the following year.
- Acquisition of high-resolution EDS mapping is of critical importance and should be encouraged by DOE.
- It is recommended to budget for implementation of EDS mapping to establish an ionomer dispersion analysis capability at ORNL.
- The researchers should determine the distribution and content of S within the catalyst layer and the changes with degradation.

Project # FC-021: Neutron Imaging Study of the Water Transport in Operating Fuel Cells

David Jacobson; National Institute of Standards and Technology

Brief Summary of Project:



Neutron imaging of water in fuel cells allows the study of dynamic water transport in the flow fields and manifolds, liquid water distribution in the anode versus in the cathode, cold start and freeze-thaw effects, and catalyst degradation induced by liquid water. Objectives of this project include: (1) studying water transport in single cells and stacks, (2) enabling the fuel cell community to utilize state-of-the-art neutron imaging capabilities to study water transport phenomena, (3) tailoring neutron imaging to the needs of the fuel cell community, and (4) improving the spatial resolution to provide more detail of the water content in commercial membrane electrode assemblies (MEAs).

Question 1: Approach to performing the work

This project was rated **3.6** for its approach.

- The team has developed a very effective approach—continual improvement of the characterization techniques and testing infrastructure, while allowing a substantial amount of time for user access to benefit the community at large.
- This team has done very well at pushing back boundaries and drawing on advances and expertise in other fields to further neutron imaging capabilities. The project features an excellent balance of instrumentation, technique, and data processing development, which benefits the entire fuel cell community.
- Using neutron imaging to identify where the water is and the dynamics of water flow in the MEA and throughout the stack is crucial to overcoming the barriers of increased fuel cell performance, durability, and water management in the stack. This activity is well integrated with other activities that are developing new fuel cell components and with stack studies.
- The principal investigator (PI) continues to improve the resolution and response time of the neutron imaging facility for detecting water in fuel cells.
- The National Institute of Standards and Technology (NIST) has an excellent tool for understanding and addressing water management in fuel cells. The tool and technique are well suited for addressing one of the critical barriers for fuel cell operation.
- The approach is clear and solid. Integration of the team with the fuel cell developers is at a high level. Resolution challenges were overlooked from the beginning of the project; the team is now trying to catch up.
- Neutron imaging work performed at NIST addresses fuel cell performance, which is directly related to the cost barrier. NIST work to improve resolution addresses one of the key barriers for neutron imaging of MEAs and, if successful, will allow one to differentiate the catalyst layer from the membrane and the gas diffusion layer (GDL). This will improve understanding of flooding and should enable improved performance. Several approaches to improve resolution are being pursued, which will reduce risk (grating approach, lens approach, and increasing detector efficiency, which will help both approaches).
- Currently, neutron imaging is one of the primary methods for determining in situ water content. The facility has provided access to many different groups, ranging from academia to industry, and from open to fee-

based private research. The analysis to date has successfully resolved the water content under various conditions and scales. One open question is the importance of understanding the distribution of water inside the MEA, particularly the catalyst layer. The extension of the facility's capability to image water with a resolution approaching 1 micron (µ) is very important, and the approach is aligned with the needs of the user base. It would be beneficial to include an overview slide in the Approach section that discusses how this advancement (1 µ resolution) is being targeted. In one approach slide (slide 6), the various test stands are mentioned along with the available reactant gases; it was not clear what aspect these test stands represent in regard to the approach for the application/development of neutron imaging related to the fuel cell community. If the focus was the development of the large-scale test stand, it may be more appropriate to focus on the approach of constructing it and the user need.
- Neutron imaging continues to be a critical technique for evaluating in situ water content in fuel cells. The approach to obtain higher resolution is good and necessary for this technique to go to the next level. Results for the overall project in terms of Fuel Cell Technologies Office (FCTO) milestones are heavily dependent on users, which might limit the applicability if the experiments are not designed correctly.
- This is a useful tool, but limited resolution has somewhat limited the value of the results generated to date. If resolution and acquisition time can continue to be improved, then this work should continue.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.4** for its accomplishments and progress.

- The progress made this year is truly outstanding; NIST achieved impressive spatial resolution in water imaging as well as sped up the time frame over which measurements can be made. The infrastructure of the facility has also been improved. The community looks forward to seeing these dramatic improvements being utilized in the future.
- The project features excellent capability and data to date. The limitations are understood and there are plans to address these; however, any work and effort that could expedite the higher resolution capability will help advance fuel cell development faster.
- NIST has enabled enough user access to support multiple presentations and publications, while improving the spatial resolution.
- The team continues to advance the time and resolution limits of this important technique for imaging water transport in an operating fuel cell.
- The progress on improving resolution has been excellent over the past year.
- The two primary aspects for the accomplishments related to the improved resolution detector were items (1) and (4) on slide 7. In regard to Milestone 1, the use of an MEA is being used as a standard to assess the difference between the sub-10 µ and the 25 µ detector. Given that the actual water content of the MEA is not known and that this method is meant to determine it, it would be better if an engineered porous test sample that was more controlled was chosen for purposes of comparison. While slide 12 clearly shows differences, it is not possible to ascertain if the data collected from the new detector is an accurate depiction of the real distribution. On slide 13, the image analysis and correction points to the importance of the uncertainty that can arise in the water content measurement. With the use of a control sample, it would be ideal to establish an estimate of this error and, in addition, with the improved image analysis and corrections, determine the overall improvement in accuracy for data collected prior to the improvement. It is unclear if users should be reanalyzing past data to reassess. On slide 14, Milestone 4 relates to the desire to study drive cycles, accelerated stress tests (ASTs), etc. The improvement in the image time versus a drive cycle or AST cycle is of key interest because water management has been shown to affect durability and the hysteresis effects in polarization will affect system considerations. It would be useful to cast the acquisition time in the context of the period of an AST or drive cycle and comment on where gains in the image time are expected to assist in these areas (e.g., cost saving for manpower or additional study capability to analyze dynamic load cycling). The use of a series of standardized engineering porous media test samples may be ideal in the development or confirmation of the new detectors and the improved resolution compared to the current ones.
- NIST has made good progress in increasing resolution; NIST has increased resolution to <10 µ, though signal to noise must be improved and time resolution is poor. It is unclear whether the low time resolution

for the grating method for increasing spatial resolution may lead to a high signal-to-noise ratio, because performance variations over the 15 hours needed for the <10 µ resolution may lead to significant variations. The four-fold improvement in image acquisition time that is to be implemented by the start of fiscal year 2015 is a big improvement.

- The accomplishments toward higher resolution are good, although still not substantially improved compared to previous years. The corrections for systematic errors are good and worthwhile, and having that integrated into the software is also a good improvement. The use of standardized hardware is also good to see. Progress was minimized due to the government shutdown. Overall, the accomplishments are on the right track, but specific accomplishments this year are slow.
- The focus this year is on improving system resolution to achieve 1 µ resolution. This requires improved gating techniques, increased flux (using focusing lens versus shutters, etc.). It is unclear how much resolution is required to achieve usable results for most fuel cell applications, and whether the extra detail will allow more in-depth analysis of the fuel cell operation.
- The milestone for high-resolution MEA water content to 1 µ is indicated at 100% complete, although it was eventually shifted to the newly formed milestone on improving high-resolution time, which is 50% achieved. At the same time, the freeze management milestone reported last year at 75% was not mentioned at all.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.7** for its collaboration and coordination.

- The NIST facility is available to all, and NIST has collaborated with quite a few fuel cell researchers. Additionally, the fact that NIST provides substantial funding makes this a good "bargain" for the DOE Hydrogen and Fuel Cells Program (the Program). It is a good example of excellent collaboration between multiple government agencies.
- The access/ability to access the neutron imaging facility is commendable. In addition, the list of users is a testament to the need to image and understand liquid water and its distribution for fuel cells from both performance and durability perspectives. The results demonstrating the application of the facility are always a high point in the presentation.
- The collaborations with universities, national laboratories, and industry are impressive and show that this is a true user facility that is being utilized by all relevant stakeholders.
- The PI is collaborating with the necessary partners to make this tool available and useful to partners who need it. The work on setting up the beam is very specific to the knowledge, skill set, and resources of the PI.
- The project features good collaboration with a large number of stakeholders including universities, national laboratories, and industry.
- By its nature, this project is highly collaborative because it provides infrastructure to support other teams.
- The project features great collaboration and access to industry partners.
- There is a long list of collaborators, both in terms of advancing the instrument capability and solving real-life fuel cell problems, with various users from industry, academia, and national laboratories. It would have been good to see one more example from the user program highlighting another interaction with industry.
- There is a very high level of collaboration, including with major original equipment manufacturers (OEMs) and researchers. It would be good to see a breakdown in terms of researchers and their beamtime (e.g., percentage for OEMs, laboratories, academia).
- Ongoing collaboration with national laboratories and universities is significant and recurring; however, there was no mention of industrial partners returning to use the facility more than one time, which would be real proof of the long-term usefulness of the method. Unfortunately, there were no examples of direct collaboration with the GDL developers, for which the current resolution would work best.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- This is one of the keystone projects of the portfolio because only neutron imaging can show where water is in operando in the stack and in fuel cell components. The project has now become indispensable to achieving the goals of the Program.
- Liquid water has been shown to play a key role in performance and durability, particularly carbon corrosion, Pt dissolution, and membrane degradation. One of the key bottlenecks has been the ability to differentiate the membrane and catalyst layers; assuming the new detectors are capable of addressing this need, this project has the potential to dramatically impact the advancement of the Program’s targets and objectives. One of the key aspects will be strong technical management of the path to the low-resolution detector.
- This project is critical to understanding water transport in fuel cells. Without this imaging capability, optimizing water transport would prove very difficult.
- Improved understanding of water movement within fuel cells can potentially yield valuable insight into future improvements on both power density (cost) and durability. The NIST facility alone will not provide the fundamental understanding required, but if these results are combined with modeling and creative experiments, as has been the case to date, then the results do add value.
- The user program highlights demonstrate the immediate impact that neutron imaging is having on fuel cell development. Ongoing technique developments will further the impact neutron imaging can have on this field.
- Water management creates analytical challenges, and the use of this experimental technique helps accelerate fuel cell development.
- Completion of the test stand for automotive-scale cells is a major step forward.
- The project is focused on improving neutron imaging rather than overcoming barriers in the FCTO Multi-Year Research, Development, and Demonstration Plan. It is an enabling technology that depends on its use to make gains in terms of FCTO milestones. Higher spatial and time resolutions are critical for continued understanding of water and thermal management.
- While not the only tool to analyze the water content of a cell, this remains an effective tool for researchers to analyze fuel cell performance.
- The project currently only partially supports the Program and is mainly useful for water transport studies. The project still did not show any progress in durability studies.

Question 5: Proposed future work

This project was rated **3.4** for its proposed future work.

- The use of a standard fuel cell for high-resolution imaging will be extremely useful for all researchers who wish to utilize this technique to evaluate their new electrode and MEA concepts. The second cold neutron imaging line will add much-needed additional capacity, and if it can discriminate water from ice, it will also add yet another nice option to the suite of possible experiments.
- The team has proposed ongoing development to extend the time and spatial resolution of neutron imaging. The future of neutron imaging looks very bright.
- The proposed future work aligns well with the advanced capabilities requested by collaboration partners. The presenter clearly outlined a path to achieve the higher resolutions.
- Work should continue on improving the flux of the beam to allow faster image capture times. It appears that capturing the dynamic response of fuel cell performance may be of more importance to OEMs now that increasing resolution makes this possible.
- The proposed cold-neutron imaging facility, which could discriminate ice from water, will be beneficial. The Wolter optics lens will be a big advance, allowing much greater temporal or spatial resolution. Collaboration with Los Alamos National Laboratory to develop a high-resolution fuel cell is necessary to take advantage of the higher resolution.

- The continued focus on improving the performance (both resolution and acquisition time) is excellent. However, the project date of 2018 for developing the new lens system appears to be excessively long. While one realizes that this is new technology, it is not apparent why this should take four years.
- Justification for the cold neutron source in terms of liquid and ice is not critical, because ice is not a major concern. The use of the microscope looks interesting, and it is critical to get the time resolution down for higher spatial resolutions. For the new improvements, it would be good to know if there is going to be an increase in any issues that cause systematic errors, and thus limit the actual improvements.
- In the future work, the use of a standard high-resolution fuel cell is shown. This cell shows the use of serpentine-based flow fields. It is recommended that for the purposes of a standard cell, serpentine-based flow fields are not used. In particular, serpentine flow fields can elicit significant in-plane pressure drops/reactant transfer across the landings, depending on the MEA used. As such, this becomes a much harder test cell to understand and design around. The use of a straight flow field is likely more appropriate for the purposes of a differential cell. In the event that this is not feasible, it may be ideal to develop both a straight cell and serpentine standard cell that then allows choice in the included mass transport mechanisms. In addition, the standard test cell should be chosen/developed such that it elicits good comparison/correlation to a larger-scale differential cell. In relation to the development of the high-resolution MEA water content based on CHANDRA, there are outstanding questions about what the comparison is between NIST's schedule for the low-resolution detector, the National Aeronautics and Space Administration's (NASA's) development, and the needs of NIST from NASA's development plan.
- It is unclear what the specific plans are. However, the emphasis on image acquisition time, in addition to resolution, is encouraging. Better time resolution to eventually capture some dynamics of local water accumulation and transport would be valuable. A high-resolution test cell with channels and lands would be much preferred to the porous flow-field concept outlined in the presentation. The effects of channels, lands, the local compression of GDL, and other constraints on the water distribution are masked by porous flow fields, but many designs still rely on channels.
- There is considerable risk in the proposed path forward, which involves engaging more and more complicated equipment in this research. The team should focus its scientific efforts on resolution and faster data imaging, while also expanding education to the industry on what features of the method could be useful in specific applications.

Project strengths:

- Strengths of this project include the following: its strong collaboration with users, its extensive users' list from both academia and industry, it is the only non-destructive liquid water imaging method currently available, novel work is being completed at the facility by users, and it has made good progress toward the development of a sub-10 μresolution.
- This is a tool that provides an in situ look at water accumulation in a fuel cell. Understanding water balance is a critical factor in design.
- The project features great collaborations both inside and outside the fuel cell community. It has very strong expertise and focus on technique development.
- There is collaboration with many industry partners. It is great that NIST and DOE help to make this tool available.
- The project features a state-of-the-art high-resolution neutron imaging facility for in operando fuel cell studies.
- The project provides a valuable state-of-the-art tool for characterizing transport in fuel cells. The team is responsive to the needs of the fuel cell community.
- Strengths of the project include its financial support from NIST, its continued progress on improving the facility's capabilities, and that it provides useful insights into fundamental phenomena.
- The project provided good diagnostics of water management for researchers in the national laboratories and academia.
- Water imaging is critical for understanding mass transport, and the project is focused on understanding this at increasing time and spatial resolutions.

Project weaknesses:

- There is a lack of a standardized porous test sample to provide confirmation for low-resolution detector/high-resolution detector comparisons. Image acquisition times are not fast enough to study realistic cycle transients. The proposed standard test cell is not consistent with industry standards. There are still significant hurdles to overcome for the high-resolution detector. There is a potential mismatch in development path timing between NASA and NIST.
- NIST is dependent on users and their ideas for understanding and improving fuel cells and fuel cell components. It would be good to see the amount of accepted versus submitted proposals and the typical reviewer base and criteria. For issues such as interfaces and ionomer and catalyst layer limitations, it is not clear that the neutron lens will reach the resolution needed for understanding.
- This technique is clearly not mobile or accessible to many partners—it will always remain a fairly expensive tool. It is unclear how useful it will be as an analytical tool when fuel cells achieve high-volume penetration.
- The team needs to make sure that the aggressive technique development does not detract from user work. Highlighting new users and more user program highlights would be strongly encouraged for the next DOE Hydrogen and Fuel Cells Program Annual Merit Review.
- The pace of degradation studies in fuel cell research is already ahead of what could be supported and explained by this diagnostic without increasing high resolution even further below 1 µ, which does not seem feasible for another year.
- Issues beyond NIST's and DOE's control (budget issues and government shutdown) have delayed upgrades and limited the availability of the imaging facility.
- The improvement in resolution appears to be leveling off, and substantial progress on acquisition time will apparently take a very long time.
- The timeline for magnifying neutron lens development is long.
- There is a lack of capacity for everyone to do experiments.

Recommendations for additions/deletions to project scope:

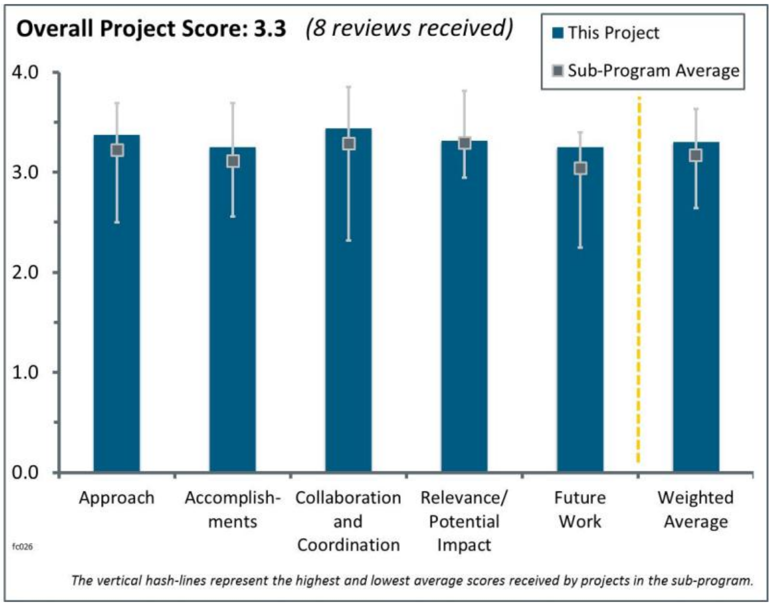
- NIST should develop an engineered porous media test sample with controlled water distribution on a sub-5 µ scale, which can be used for benchmarking images quantitatively. NIST should also develop a straight flow field standard test cell rather than a serpentine-based cell and benchmark the straight flow field test cell with a similar, larger-scale differential cell.
- NIST should prioritize either 10- or 1 µ resolution work. It should also elevate awareness of the method capabilities to GDL developers and stack developers. In addition, it should reassess the efforts required to maintain the fuel cell infrastructure for automotive-scale testing and, if utilized at a low rate, redirect the efforts.
- The PI should elaborate on which attribute is more important to OEMs—resolution or response time.
- The team should think about adding some flexibility into the standardized hardware in terms of compression, pressure control, and utilizing next-generation material sets.
- The project team should try to accelerate the schedule on the new lens system.
- Researchers should pursue more of the same type of work.

Project # FC-026: Fuel Cell Fundamentals at Low and Subzero Temperatures

Adam Weber; Lawrence Berkeley National Laboratory

Brief Summary of Project:

Primary objectives of this project are to understand transport phenomena and water and thermal management at low and subzero temperatures using state-of-the-art materials and to elucidate the associated degradation mechanisms due to cold and cool operation. Improved understanding is expected to enable U.S. Department of Energy (DOE) targets to be met with regard to cold start, survivability, performance, and cost. Water management is examined in thin-film catalyst layers and various fuel cell components.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.4** for its approach.

- This project uses a solid approach of combining ex situ constitutive property measurements to obtain the parameters of the individual components to input into the component submodels and in situ fuel cell testing with advanced diagnostics to validate the two-dimensional (2-D) cell model. The researchers are focused on the fundamental thermodynamics, transport, and kinetics that govern fuel cell performance and cover the range of relevant operating conditions.
- The approach combines in situ/ex situ diagnostics and measured data as validation for submodels and then as input for the cell model. This provides a solid basis for the provision of input parameters and confirmation of the physics submodel per submodel. The overall validation being done using cell data and various in situ studies provides a range of conditions appropriate to test the included physics/phenomena.
- The approach is well organized, with multiple partners performing specific tasks.
- The approach for model development and validation is sound.
- Developing models via model-experiment comparisons at both the cell and component levels appears to be an effective approach. However, the land/channel 2-D cell model only applies to differential cell conditions. It is insufficient in simulating down-the-channel distributions of current and water, which are normally non-uniform when a cell starts at cold condition.
- The general approach of applying ex situ and in situ diagnostics to develop inputs for a cell model that is then applied to explain trends observed in operando is sound. Two recommendations:
    - The project team should not use serpentine flow fields in any aspect of this project, because of the known problems with U-bend water accumulation and reactant short-circuiting. A flow field with pure counterflow in the active area (developed by General Motors and used by Los Alamos National Laboratory and others) eliminates these issues; produces nearly one-dimensional (1-D) distributions of current density, temperature, concentration, etc.; and is much easier to model and understand. Moreover, perhaps most importantly, this geometry closely approximates the design of most application hardware.
    - The project could benefit from closer collaboration with a system integrator or original equipment manufacturer (OEM), who could provide insight into issues related to full-size stack hardware.
- The connection of diagnostic data and materials characterization to the developed cell model is still not as clear as one would like. For example, regarding the “new” anode gas diffusion layer (GDL) versus “baseline” studies, there is GDL characterization and cell-level water characterization, but there is no clearly presented example of a model plus varying GDL properties predicting the trends. Similarly, to

address water management in an operating cell, transient and spatial (at least the proposed 2-D + 1-D) effects should have been considered in the model from the beginning.
- Stack studies are defined in Task 3 but not in the milestones. It is unclear whether the model is being compared to stack data.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- The demonstration of the differences between the improved and baseline GDLs for the nanostructured thin-film (NSTF) catalysts is a key finding. The identification that the kinetic nucleation plays a key role in the onset of freezing versus a purely thermodynamically controlled process is key to improving freeze start capability.
- The additional experimentation and testing is great to help validate the model.
- Some interesting data is being collected and no doubt progress is being made, but some of the claimed accomplishments are not substantiated by the material presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review. Specifically, there was no evidence of a validated steady-state model over a full range of operating conditions. The water balance data for different microporous layers (MPLs) is interesting and shows how low temperate performance can be improved. It is not clear whether the model predicts these improvements or how the GDL properties should be further modified to make additional performance improvements. Validating that freeze kinetics are important is a nice, if not surprising, result. It was not clear whether the model predicts the isothermal and adiabatic freeze start experiments from United Technologies Research Center (UTRC).
- The project's GDL characterization is quite comprehensive. Water droplet detachment velocity appears to be a characteristic parameter suitable for new GDL screening. Easier droplet detachment results from lower fiber density and thus preferential water pathway; however, the model still uses Darcy's law for liquid water transport in GDL.
- Identifying the importance of anode GDL transport characteristics for NSTF water management is valuable. The GDL ex situ characterization is adding some quantitative information for these particular materials, but the trends and interpretation are essentially the same as a number of previous studies. There was no mention of the anisotropy of transport properties of the GDLs.
- The team has developed a good modeling framework and conducted tests to validate the model. The team now has to exercise the model to improve the performance of the NSTF electrode; it is unclear how this model will be applied to solve this remaining challenge.
- This project has made a clear impact toward the key mechanisms that limit NSTF cold start performance. However, the quantitative impacts against DOE metrics were not disclosed.
- Regarding slide 13—other DOE projects and recent literature (e.g., Caulk and Baker, *Journal of the Electrochemical Society*, 2010) have shown that through-plane thermal conductivity and an effective dry diffusion coefficient have controlling influence on GDL water transport and accumulation. The reviewer wonders if these parameters been considered in the performance of the baseline and improved materials, with and without PTFE. Regarding slide 14—it is suggested that the project team apply some effort to studying the patent literature. A number of companies have shown that in-plane variations in GDL properties can significantly improve fuel cell performance. Regarding slide 18—this experiment seems to be based on the assumption that the MPL controls the rate of liquid water transport. It is unclear how the researchers know that the MPL does not promote water transport in the vapor phase, as has been reported in the literature.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- This project has excellent collaborations among national laboratories, universities, and industrial partners for component characterization and cell diagnostics. It is well coordinated in terms of getting data for modeling.

- There is significant collaboration on this project. The presenter did a nice job of describing the interactions and why specific collaborators were selected.
- The project has a great team working together from industry, academia, and national laboratories.
- The change to an adiabatic cell design is positive, in that it implies better connection between the effort to understand water transport and the experimental design.
- There is a strong list of collaborators for the project. There are a number of researchers that are linked to no-cost work on Nafion® thin films—it would be useful to comment on how this work will be included and to what degree it is believed to be important/a critical path. The project appears to lack the inclusion of an OEM or stack manufacturer (in addition to UTRC); it would be beneficial to consider including another for added perspective.
- The project is benefiting from the contributions of many collaborators, especially in the area of advanced diagnostics and experimental methods. UTRC is the lone OEM collaborator, and it is not clear whether it is providing guidance that is representative of the broader OEM community on the most critical issues that should be addressed.
- Collaborators are well recognized for their expertise. A GDL supplier should be engaged to consider the manufacturability and cost aspects of novel concepts. Also, the stack/system level input from UTRC was not obvious in the presentation.
- Generally this is a strong group, but the team could benefit from close collaboration with an OEM water management expert.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- This is a nice project to help understand the fundamentals around water management, and it could help accelerate technical advancements.
- Cold start issues related to thin electrodes remain a critical issue in the state of the art.
- This work is excellent and one of the projects pushing the envelope in understanding fuel cell transport understanding. The team should use simpler hardware designs that are more representative of real systems.
- The fundamental understanding of freeze-thaw and of NSTF water management issues will be of strategic value to the community as a whole. Without temporal and spatial effects in the developed model, its application to improving water management in an automotive cell will only be to provide qualitative trends.
- Robust cell performance at low and subzero temperature is essential to the successful commercialization of fuel cell vehicles. Although the project is focused on NSTF electrodes, which have shown poor performance in cold environment, the learnings on other cell components (e.g., GDL and membrane) will be applicable to the cells utilizing conventional electrodes with dispersed catalysts.
- The relevance of this project is limited by its focus on NSTF-based membrane electrode assemblies (MEAs). The biggest challenge to enabling low-Pt-loaded MEAs is the local O_2 transport losses in the cathode. It is not clear how this critical issue is being addressed within this project. Also, it is not clear how the Nafion morphology studies will help address any of the key problems currently facing OEMs. There is no evidence that the rate of water transport from the thin electrode layer into the membrane is impacting low temperature performance, and, even if it is, it is unclear how the morphology studies being done will help reduce that limitation.
- The project focuses on aspects related to the key barrier for inclusion of the NSTF catalyst into commercial products. In addition, the project addresses aspects that may be related to the loss seen in low-loaded catalysts. It would be ideal to add additional catalyst layers, such as high-surface-area or low-surface-area Pt/C catalysts, in order to elicit different mechanisms for water transport and subzero operation.
- The relevance of this project is not aligned with the Fuel Cell Technologies Office focus area; this project is addressing the performance issues of NSTF, which is not the primary gap area for fuel cell technology as a whole. Performance challenges of NSTF, stack water management, and start-up issues are not critical path items for supported catalysts. All automotive OEMs have shown that the current system can meet the performance goals set by DOE.

Question 5: Proposed future work

This project was rated **3.3** for its proposed future work.

- The proposed future work includes developing a 2-D +1 down-the-channel model and characterizing a traditional dispersed catalyst, which is in the right direction toward finding optimization/mitigation strategies for fuel cells in real-world applications.
- The project covers many of the previous years' comments. Expansion of the traditional CLs to consider the effect of different types of carbon support may be well suited. In addition, development of a list of key inputs/outputs from the model would be very beneficial. Furthermore, slides discussing the confirmed submodels and the associated validation could be included to demonstrate the successful confirmation for key areas, such as water management.
- Much of the future work is relevant. The team should especially pursue "Soliciting input and advice from automotive companies." It would also be good to see the team prioritize "Examining properties and uptake with low-EW ionomer and ionomer thin-films" of dispersed catalyst layers. Validating the transient model, especially for NSTF electrodes at cold start conditions, should also be a priority. The only future work that should be eliminated is studying the "interfacial resistance and membrane morphology with different environments."
- The future work is very ambitious, considering the project is already extended and many of these objectives have carried through the project since it began. It is appropriately focused, but the timeline and feasibility are unclear. Many of these fundamental questions will linger. Perhaps a sensitivity study can help to optimize resources. Also, this project should consider the inner layer presented by 3M.
- The future work is largely focused on additional characterization and model improvements. There should be more application—identifying materials solutions and operating strategies to improve cell performance.
- Because there are a lot of pieces to this project, it would be helpful if the future work also referenced the work plan tasks defined in the project approach.
- The proposed future work is generally solid, but the research team should consider a more even split of the effort between NSTF and conventional electrodes, despite the originally proposed project scope.
- "Understanding stack location effects" (and others) are outside the scope of this fundamental activity, and that is not a key challenge area. The project is almost ending, so the focus needs to be on exercising the model to understand how the performance of these thin catalysts layers can be improved.

Project strengths:

- The project has the following strengths: (1) a fundamental approach to studying water management and sub-zero operation; (2) various levels of inputs, diagnostics, and validation; (3) strong collaboration between various organizations; (4) addresses the impact of both the catalyst and the GDL; and (5) considers different mechanisms for the formation of ice.
- There is a clear linkage between characterization and modeling. Investigators have applied and developed state-of-the-art methods toward the critical aspects of the problem.
- The project has a great team with a strong publication record. It is clearly starting to close the loop on fundamental water management issues.
- The project features strong fundamental modeling and physics, coupled with good experimental characterization.
- Strengths of the project include its solid approach, very strong team, and access to world-class experimental and modeling facilities.
- The combined modeling and experimental approach and strong coordination between highly capable modelers and experimentalists are the project strengths.
- The project investigates fundamental understanding of key barriers.
- The project features a good team and strong fundamentals.

Project weaknesses:

- The project has the following weaknesses: (1) importance of interfaces between various components and the role in water management/subzero operation; (2) lack of a stack developer or automotive OEM; and (3) unclear leverage of thin-film tests from no-cost partners, and an inconsistent timeline versus the critical path.

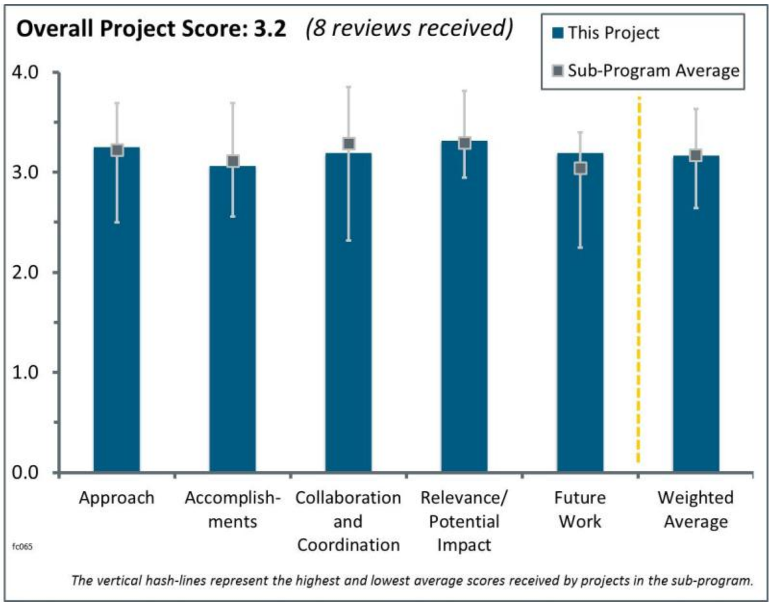
- The project seems very focused on basic science; there is not enough application of what has been learned to investigate what a next-generation material or future operating strategy should be.
- There is a lack of direct input from automotive OEMs. Models, to this point, seem to focus on explaining data rather than driving mitigation strategies for key issues and materials and design improvements.
- Proton conductivity on wet Pt is a difficult challenge, and this model requires a validated mathematical description of this phenomenon.
- The researchers should have a more direct relationship with a water management expert working on full stacks and systems so the fundamental experiments/modeling comprehend "real-world" issues.
- With the proposed future work, this project does not seem to have a weakness.
- The focus area is not the critical path.

Recommendations for additions/deletions to project scope:

- The droplet detachment velocity sensitivity of the improved GDL with and without PTFE relative to the baseline is intriguing. If the materials cannot be revealed, it is essential that the key parameters involved are investigated. Neutron imaging also seems like an ideal validation tool. There must be a tradeoff related to passively shifting the water balance to the anode during normal operation. It is unclear whether this is really a solution to the cold start issue from an overall system efficiency point of view. This project should consider the inner layer presented by 3M.
- The researchers should consider the use of different surface area carbon supports when considering conventional Pt/C layers (including low loaded). They should also include an additional OEM or automotive partner.
- The team should remove studying the interfacial resistance and membrane morphology with different environments from the future work. Instead, it should focus on dynamic testing and model validation.
- Because the NSTF electrode is not ready for automotive application in the foreseeable future, more work should be done on the electrode with traditional dispersed catalysts, including quantifying liquid water distribution.
- It would be nice to see additional testing for the transient states.

Project # FC-065: The Effect of Airborne Contaminants on Fuel Cell Performance and Durability

Jean St-Pierre; Hawaii Natural Energy Institute



Brief Summary of Project:

The objective of this project is to identify and mitigate the adverse effects of airborne contaminants on fuel cell system performance and durability. The adverse impacts are mitigated by providing input into air filter specifications and into fuel cell material selection, design, and operation. The Hawaii Natural Energy Institute (HNEI) obtained detailed characterization information about the performance impact of eight contaminants to support the development of mitigation strategies.

Question 1: Approach to performing the work

This project was rated **3.3** for its approach.

- The project features a clear approach with well-defined goals and barriers.
- The systematic approach to identify and characterize potential airborne contaminants is sound.
- The project is focused on durability and performance issues and addresses key barriers to fuel cell commercialization. Recovery techniques are being investigated, which is appropriate. The project has focused on Pt catalysts at relatively high loadings in comparison to U.S. Department of Energy (DOE) targets, though pure Pt catalysts are unlikely to meet the cost and loading targets. The initial data on Pt have been useful, but as the project progressed the focus should have shifted to lower loadings and current state-of-the-art alloy catalysts (or nanostructured catalysts derived from alloys) at low loadings (comparable to DOE targets). The use of methanol as a model contaminant for water scavenging of all the organic impurities is not a good choice (slide 14). Methanol is completely soluble in water, where several of the organic contaminants (propene, acetylene, bromomethane) only have slight solubility or are insoluble (naphthalene). Removal of these species by water should be quite different than removal of methanol.
- The approach (no overlap with air contaminants that have already been studied, selection of contaminants based on probability in air and effect on membrane electrode assembly [MEA]) has been established in prior years and improved this year with some incorporation of low-loaded cathodes. The use of a gas chromatograph to analyze cell effluent is an improvement. The problem with the project is that low loading (0.1 mg/cm^2) has not been fully incorporated for all contaminants, and the project may not get a chance to complete low-loading tests. Because it is known that voltage losses are different for low-loaded cathodes, it is reasonable to say that contamination mechanisms may be different for low-loaded catalyst layers.
- The project has addressed a large list of potential airborne contaminants that are a potential barrier to the use of fuel cell systems in certain regions. Within the approach, each contaminant is tested individually—comments or analysis may be beneficial to rule out the potential for reaction between different contaminants on the catalyst surface.
- Systematic study of the classes of contaminants will lead to improved understanding of the types of poisoning and recovery methods. Perhaps this effort may guide development of advanced air filters that target removal of particularly nasty airborne contaminants. While it is understandable that NO_x, SO_x, and NH_3 are excluded due to the vast research out there, it would be good to include them in very brief form to set a baseline to which the other contaminants can be referred.

- The applied strategy needs significant improvements. The only way to learn how trace levels of organic impurities may affect interfacial properties is to first apply a surface science strategy that incorporates a variety of spectroscopies (e.g., FTIR [Fourier Transform Infrared] for monitoring adsorbed oxidation products) and electrochemical measurements on well-defined surfaces, and then transfer the knowledge gained to real systems. The same applies for the effect of Ca_2+ and/or $CaCl_2$ and/or SO_4-, which is of paramount importance for the development of fuel cell systems. The systematic addition of these “impurities” in clean electrolytes and the monitoring of changes in adsorption/reactivity properties of the three-phase interface is the only way to develop a true understanding of the role of these impurities on the oxygen reduction reaction (ORR) and peroxide production.
- The selection of contaminants for research in this project appears to be somewhat arbitrary. Most impurities do not seem to be of particular concern, occurring rather sporadically; some are rather exotic.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.1** for its accomplishments and progress.

- The team has achieved excellent findings with regard to the Pt loading and contaminant effect. There was a clear presentation of the contaminants and how they respond within the cell over time.
- The team has done well with its focus on recovery from airborne contaminants, with several sound guidelines and discoveries that will benefit the fuel cell community as a whole.
- Previous targets seem to have been met, and the project is on course to meet current milestones with minimal delay.
- The project has demonstrated that for the contaminants considered, the primary impact is on the catalyst surface and not on impacts on the porous media. It would be useful to consider if there are any suspected compounds that are known to bond to carbon that may alter wettability or contact angle and would result in a different conclusion. In slide 8, commenting on the role of current density on Pt surface area, basis may assist in eliciting the turnover effect that happens when moving to lower loadings. Regarding the organic species inhibiting the oxygen path to water, it is unclear whether this is due to competitive co-adsoprtion effects, and, if so, whether it is possible to consider this effect as a change in the energy necessary for adsorption as a modification to existing platinum oxide analysis/ORR pathway models. The test data from the segmented cell are run in constant current mode; in this mode, the cell segments will experience a voltage response in order to produce the appropriate amount of current. In essence, each cell becomes more or less efficient depending on its local conditions. However, if the mechanism of the contamination is electrochemical, versus chemical, differing responses could be expected by a change in the local potential. As such, perhaps a constant voltage test may be more appropriate to controlling the state of the surface of the catalyst related to the contamination. For foreign ion contamination, it is unclear if there has been confirmation of which compounds tend to de-protonate versus ones that are simply water solubility and have the potential to be solvated within the water phase of the ionomer; this may be important for compounds that are doped into the ionomeric materials for membrane durability.
- The project has obtained data on a variety of contaminants and provided useful data to the community. The 1:1 correlation between the kinetic loss and what is attributed to a mass transfer loss on slide 7 is questionable. It appears more likely that the “mass transfer” loss is a kinetic loss for which the researchers are not correctly accounting. Other tests to determine if this loss is mass transfer related would be beneficial (limiting current measurements, different gas compositions).
- The principal investigator (PI) presented data that may serve as a foundation for understanding the effects of organic impurities on the ORR and peroxide formation, as well as the effect of peroxide formation on membrane degradation. The PI has not pointed out how reproducible these data are. This is very important because the effects of impurities are usually difficult to reproduce, even on single crystal surfaces. The proposed mechanisms are rather speculative and more in situ information is required. The interesting part is the role of cations on interfacial properties and how hypothetical (but as of now unproven) accumulation of cations at the interface is competing with the adsorption of anions—in particular, CO.
- Progress in the project has been moderate, which may in part be related to significant underspending of the project funds; the project is 80% complete based on schedule, with only approximately 56% of funds spent. The focus has been on collecting test data with relatively little in-depth interpretation of the mechanism of

performance loss and recovery or development of viable mitigation strategies. Performance recovery protocol based on cycling up to 1.2 V is unrealistic.

- The project still does not understand whether lower loadings introduce different contaminant mechanisms. Unfortunately, the standard Pt loading is 0.4 mg/cm^2, and this is the basis for many of the percent loss numbers. For many contaminants, the project is still trying to understand contamination mechanisms. However, at least some work has been done for at least one concentration for each contaminant at low catalyst loading. Good work has been done to show that for the contaminants in the project, the mass transport losses are associated with contamination on the Pt surface (adsorption). The relationship of contamination to H_2O_2 has been discussed in the literature. Data may be more useful if more concentrations were investigated. For example, the table on slide 6 shows very high acetylene concentration and thus high degradation.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- A wide range of collaborators have contributed. It appears that General Motors contributed with respect to test stand design and modeling of cation contamination. Ballard, the University of Connecticut, a few defunct organizations (UTC Power, ClearEdge Power), and numerous other governmental and supplier organizations have all contributed information. It appears that the investigators have done a thorough job of gathering information from as many sources as possible.
- Collaboration is excellent and partners are well coordinated with the leading PI.
- The strong partners and collaborations continue to be a strength of the project.
- Activities seem well integrated between collaborators; the lack of explicitness in the presentation makes this harder to judge. In giving the score, the reviewer has assumed the lack of individual organizations' slides means the project functions as a unit, which is the best way it can be run. The lack of short stack testing to see how recovery from the most common contaminants is affected by an extended system is an area for improvement.
- There is good collaboration with those in the project. Collaboration with automotive original equipment manufacturers (OEMs) and catalyst developers would have been useful.
- Collaboration exists, but the collaborators' roles were not clearly discussed and the impact of their contribution was not mentioned.
- There are many organizations involved in this project. Though difficult to assess, the degree of effort and coordination seems sufficient.
- The project includes two OEMs—Ballard and United Technologies Research Center. It would be advisable to have an additional automotive partner with a high level of involvement. The need to go to lower-loaded catalyst layers will be impacted by the tolerance to airborne contaminants due to competitive co-adsorption- and turnover-related phenomena; this is primarily the direction needed as the automotive industry nears commercialization of fuel cell fleets.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- Air contaminant effects are relevant to understanding fuel cell degradation. There are also cost considerations. If certain contaminants need to be scrubbed or filtered, the extra equipment needs to be considered in calculating the cost of a fuel cell system. Another alternative would be the addition of Pt or active area to compensate for the extra expected performance degradation due to air contaminants. The work is also relevant because at this stage it does not overlap tremendously with OEM efforts, especially for contaminants that have not been exhaustively studied in the literature. It is easier for OEMs to have national laboratories and universities survey a wide range of contaminants.
- This project is relevant to Fuel Cell Technologies Office (FCTO) goals, as described in the FCTO Multi-Year Research, Demonstration, and Development Plan.

- This is a unique study in the fuel cell community that has already yielded valuable information on the impact of and recovery from airborne contaminants.
- The effect of airborne contaminants on the catalyst layer could potentially be a huge issue with the rollout of a fuel cell fleet, depending on the locale. Much of the effect of catalyst-based contaminants will only become more influential as the industry drives to lower loading. It would be advisable to consider adding low-loaded catalysts to the test protocol. In addition, the generated data can differentiate between contaminants that are reacting from an electrochemical versus a chemical pathway. In this sense, it should be possible to construct a data table that consists of the contaminant, the reaction pathway, the rate of reaction or adsorption, and the method of cleaning with the associated rate. This table would provide the capability to cast the data into other performance models such as the Argonne National Laboratory system model to establish the design/cost effects on the fuel cell system.
- This is an excellent project—understanding which contaminants impact performance is imperative. The team should have a slide that indicates where the contaminant is typically seen, how likely it is to be encountered, and what filtration would be required to remove it.
- The role of impurities in electrocatalysis—particularly in the OER—is huge, affecting both the activity of catalysts and the stability of interfaces in hostile electrochemical environments. The PI demonstrated that a small amount of organic impurities and cations have a dramatic effect on reactivity and peroxide production, and consequently the stability of Nafion®. However, the project fails to address an equally important issue— namely, how the very same impurities may affect the stability of the support and the catalysts.
- The project is good at identifying possible sources of performance-diminishing contaminants, which is an important first step. More focus on the development of mitigation and recovery strategies (rather than merely ceasing to supply the contaminant) will enhance the impact. So far, there does not seem to be a focus on the influence of contaminants on MEA degradation/durability (not just poisoning effects), though it is proposed in future work.
- The project helps identify impurities that may be a concern; however, more relevant catalyst materials and loadings are needed.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The database is a key aspect of the future work and is valuable to many different groups with the industry and fuel cell programs. The format of the database is key and certain key information should be included. The solubility of the airborne contaminants should also be assessed because it will be a key aspect to including the reaction mechanisms and appropriate mechanistic delivery to the Pt surface. The effect of the peroxide production on the membrane should be identified, and consultation with the U.S. DRIVE Partnership's Fuel Cell Tech Team and other automotive and industry partners should be done on the appropriate membrane durability protocol. Consideration of the peroxide production/airborne contaminants on the seals for the cell should also be pursued.
- The project features a well-defined and relevant plan. Disseminating the data to industry would be very useful. Mitigation strategies will also be important—it will be good to see these.
- Further insight into the mitigation of contaminant effects is a key aspect of the future work, as is a mechanism to disseminate the project database to industry.
- The proposed future work will focus on a key need for helping automotive fuel cell commercialization—adding robustness to the system toward airborne contaminants. Perhaps the only thing to add is the possibility of crossover from these contaminants to the anode side of the MEA, where a much lower Pt loading is more at risk to contamination. Therefore, the effect of these contaminants on the hydrogen oxidation reaction would also be a great addition.
- The project has correctly identified that many measurements have to be repeated at lower loading. The investigators have indicated that they are racing to achieve this before the end of the project. Similar to the other contaminant project, this project is seeking to disseminate a large database to industry in order to assist with filter designs that will be needed to prevent air contamination of a fuel cell stack.
- The future work plan is logical and has achievable goals.
- The project is concluding in nine months. The work proposed is appropriate to complete the project.

Project strengths:

- The main strength of this project is its thorough approach to testing fuel cell performance with selected contaminants. The mechanism of the increase in peroxide yield as a function of catalyst contamination is convincing.
- Strengths of the project are the well-defined contaminants, impact on cell performance over time, recovery of the cell after contamination, and future mitigation plan development.
- The new mitigation and recovery strategies are an important result and highlight the strength of the project approach and expertise of the team members.
- The project features an extensive database of contaminants. Other strengths include the identification of electrochemical and chemical reaction pathways, identification of distributed reaction effects in the segmented cell, and potential for the identification of specifications for contaminants in the air stream.
- The PI is highly qualified to lead the project. The experiments are reasonably well organized and most of the conclusions made are in line with experimental observations.
- The project has widely surveyed a vast number of air contaminants. It has a considerable breadth of collaborators. Efforts do not overlap greatly with OEM activities.
- The project features a systematic, thorough study, as well as good collaborations.

Project weaknesses:

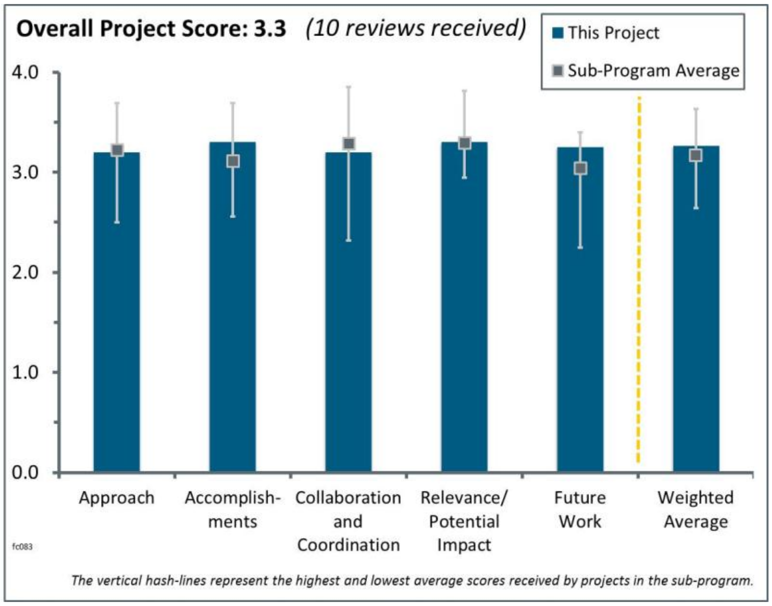
- The project still needs to complete testing at low Pt loading on the cathode. It could possibly benefit from looking at some contaminants at lower concentrations. There is still some effort needed to identify mechanisms for some contamination. The project needs to clarify contamination mechanism pathways.
- A weakness of the project is the lack of consideration for low-loaded platinum group metal (PGM) or non-PGM catalysts. Other weaknesses include the competitive co-adsorption effects (interaction) between contaminants, and the consideration of the effect of airborne contaminants in the dissolved phase on the MEA seal materials.
- There is limited emphasis on the mechanism of performance degradation. There are also some errors in the interpretation of the causes of performance loss.
- The lack of a clear plan for dissemination of the project’s findings to industry is a major weakness of the project.
- There is still a lack of the fundamental knowledge that is required to understand, and ultimately predict, the role of impurities.
- Hopefully this will be amended in future work, but efforts need to be made toward mitigation (filters) and recovery. There is also a lack of short stack “real-life” validation.

Recommendations for additions/deletions to project scope:

- It would be good to see added to the scope the effect of common poisons to the anode, unless crossover can be proven to be nonexistent. The team should also include common contaminants such as NO_x, SO_x, and NH_3 in brief form to set a baseline to compare to the literature.
- The researchers should include the effects of low-loaded/non-PGM catalysts, include interaction effects between contaminants, categorize data as per recommendations in other comments, and consider the effect of dissolved contaminants on seal materials.
- HNEI needs to continue testing at low Pt cathode loading. In case some contamination mechanisms are not linear with concentration, low concentrations should also be tested.
- Future work should concentrate on scientific aspects of performance degradation, the understanding of which is required for the development of effective mitigation strategies.
- The team should add an overview slide identifying where the selected contaminants are likely to be encountered.
- If the project is going to be continued, a surface science approach must be a part of this project.

Project # FC-083: Enlarging Potential National Penetration for Stationary Fuel Cells through System Design Optimization

Genevieve Saur; National Renewable Energy Laboratory



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Brief Summary of Project:

The goal of this project is to build an open-source tool (Distributed Generation Build-out Economic Assessment Tool [DG-BEAT]) that helps combined heat and power (CHP) fuel cell developers, end users, and other stakeholders determine the appropriate sizing to reduce cost; facilitate integration into commercial building control and heating, ventilation, and air conditioning (HVAC) systems to maximize durability; compare performance relative to incumbent technologies; determine optimum system configuration; and evaluate potential market penetration.

Question 1: Approach to performing the work

This project was rated **3.2** for its approach.

- The approach involves the development and dissemination of an executable generic CHP system installation and operations/emissions analysis tool with several input modules. The model will have broad applicability.
- This project builds an open-source tool that will enable an economic analysis for CHP systems, optimization of the system configuration, and essentially establishment of the business case for fuel cell CHP systems. This is an excellent concept and sound approach.
- The approach to the model formulation was good. The project uses a sound, realistic approach and analyzes a vast amount of data. The excellent additions to the model this year make it even more useful.
- The approach is conducive to delivering a compiled Windows executable version of the model to the User’s Group, and it includes 1,024 building energy load profiles.
- A valuable database has been established for siting fuel cell systems.
- The approach for engaging the community through development of the open-source application tool is ambitious and clear. The practical engaging of real industrial entities seems challenging and limited to only several names.
- The general objective of the project is of great interest to help system designers propose the right fuel cell system, depending on the location and the building. The proposed approach appears to be correct, but there is some lack of explanation about the fixed and variable parameters offered to the software users and how optimization between fuel cells and batteries is handled.
- The approach is to develop and evaluate a model for assessing stationary fuel cell performance in supplying energy to buildings. Efforts to develop, evaluate, and distribute the model to users groups are all on schedule. A significant new component of the approach is the addition of information and modeling to address emissions reductions. However, the results of this effort in the optimization calculation are not yet included.
- The reviewer admits to being confused by this project, and this is reflected in the reviewer’s scores. The U.S. Department of Energy (DOE) goal as stated on slide 3 is to, by 2020, develop medium-scale CHP fuel cell systems that achieve 50% electrical efficiency, 90% CHP efficiency, and 80,000 hours of durability at a cost of $1,500/kW for operation on natural gas, and $2,100/kW for operation on biogas. It is not clear how the development of the DG-BEAT tool helps to achieve that goal. That needs to be explained by the PI

in much more detail. This could be a poor selection of the DOE goal being addressed. If the goal is to support implementation of CHP systems in the marketplace, then this model would be quite useful. However, that is not what the selected DOE goal states.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- The research team has made excellent progress. The addition of emissions control benefits is useful and important. Sizing optimization work is very good. This work does a good job of addressing the load profile in modeling optimum performance. The model now has good coverage both for geographic and temporal variability.
- Significant accomplishments include the following:
    - Implementation of greenhouse gas and criteria pollutants emissions reporting—t including hourly emissions profiles and an emissions minimization control strategy.
    - Implementation of non-predictive load-following strategy. Foundations are in place for higher resolution demand profiles (<1 min) for better examination of system response lag.
    - Implementation of new building profiles for 16 building types in 16 climate regions and 3 building vintages.
- The project team made good additions to the tool with the emissions data and more building profiles.
- This year's additions to the model greatly improve its utility.
- It seems like there has been significant progress in the development of the tool by integrating new parameters in the model. New results have been presented. However, the slides are not very easy to understand. Fortunately, the presentation helped one better understand the possibilities of the model. It is unclear how the extrapolations are done to adapt to the real requested powers. There is no information on durability even if it is critical for stationary application. It is also not clear how optimization of the hybridizing level is handled. Regarding emissions, particle matter of less than 10 µ diameter (PM10) is mentioned in the Approach but not integrated in the Accomplishments, even though PM10 is important regarding health issues.
- The progress has been excellent. The implemented control strategy models fuel cell systems' response and also allows the use of different fuel cell types. A selected user group is identified to test the model and detect areas for improvements. In order to understand the accuracy of the model, a sensitivity study around the different system elements and input parameters would be beneficial.
- Progress on modeling is very good—the model is live, new blocks were added, and resolution was improved. It would be good to see more sensitivity testing with the different case scenarios not limited to single numbers or one company.
- The model is sophisticated; however, it is hard to see a "general" strategy among all of the data.
- The project ends in October 2014. All milestones have been met except for final model delivery, which is on track.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- The coordination with partners is solid—the team started to refer to the model and results directly into conversations with industry. Developing work-case scenarios and educating partners on how to do the analysis needs further work.
- The project features excellent collaborations from the following: University of California, Irvine; Lawrence Berkeley National Laboratory; Strategic Analysis, Inc.; Battelle; IDIQ; and several end users who are referred to as the User's Group. The strong collaboration with the User's Group draws from different types of fuel cells, cost and systems analysis, and building energy experts.
- The project features a good mix of many collaborators with different/complementary backgrounds.
- The broad involvement of industrial users to provide feedback is very valuable. However, the commitment level of the User Group is not clear.

- The collaboration and coordination appear to be correct. The User's Group should be enlarged with fuel cell producers and end users.
- There was some brief discussion of collaborations, but the presentation did not provide much detail. Moreover, there was limited discussion on what value was added as a result of collaborations with other national laboratories and vendors.
- It is not clear how involved the User's Group or manufacturing analyses projects are in the project. The presentation identified collaborations, but the involvement was unclear.
- It is not clear what distinguishes a "core" partner.
- Additional collaboration with industry is needed to help validate the model.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- The analysis is well done and generally aligns with the DOE Hydrogen and Fuel Cells Program (the Program) and DOE research, development, and demonstration (RD&D) objectives. Upgrades to the model this year greatly improve its relevancy.
- The project aligns well with the Program and DOE RD&D objectives and has the potential to advance progress toward DOE RD&D goals and objectives.
- The project is well targeted and beneficial to the research goals of the Program.
- The model facilitates analysis of more than 1,000 CHP scenarios, providing a basis for system selection and design optimization.
- The project develops a tool that enables the optimization of CHP system configuration and cost based on building energy use and thus indirectly supports the DOE CHP fuel cell system targets.
- This project aligns well with helping one understand the impact fuel cells could have in various applications.
- Once the model is experimentally validated, it will contribute to the dissemination of the fuel cell technology in buildings by demonstrating the energetic and economic advantages of this technology. A great impact will only be possible if the documentation is clear enough for one to use this model quite easily with a huge amount of possibilities.
- This project seems to lead to a valuable tool; however, it still has to be proven and validated.
- This is a valuable tool for evaluating the potential for a system in a building, but that does not mean it will help meet the DOE performance goals defined in slide 3.
- Alignment with the DOE objectives is not fully clear or quantified. Introducing some metrics would be useful.

Question 5: Proposed future work

This project was rated **3.3** for its proposed future work.

- This project is a springboard for broad industry involvement in beta testing and dissemination.
- The proposed future work is good and a straightforward continuation of the efforts.
- There is a good pathway forward to completing the tool and improving its database.
- The proposed plan forward is logical and addresses the remaining challenges adequately.
- The project has a good plan for future work.
- The proposed work is in line with the objective of the project. Quality control of the different modules and field validation of an existing installed system should be the main focus of the future work.
- Overall, the proposed steps for future work were well described and relevant to the project goals. There was a brief discussion of model validation without many details on how it will be carried out. It is concerning that there are challenges in doing a model validation without better insight on parameter sensitivity and uncertainty. The researchers should consider a model performance assessment (particularly a sensitivity analysis) as a part or even in place of the model validation effort.

- The future scope is well thought through. More prioritizing is recommended toward model validation and testing and engaging the user group in this activity.
- The proposed future work will continue to enhance the utility of the model. The researchers should make an effort to make the model more readily available.
- The proposed future work should be expanded to include more validation of the models, either through test cases or collaboration with an industry partner.

Project strengths:

- The researchers have made timely and significant progress. The work is very relevant to the research goals of the Program. The consideration of avoided emissions (CO_2, SO_x, NO_x), along with the cost/value of the energy produced, is an important and useful addition. The work is well targeted to the needs of users. The software provides users with a broad range of parameters and scenarios and has a well-structured graphic interface.
- The model appears to be very flexible and not limited to already existing components in the National Renewable Energy Laboratory database.
- The project is built upon a solid foundation and well thought through. The component sizing work is worth further pursuing.
- The modeling approach was excellent. This should be a valuable tool for modeling the efficacy of fuel cell CHP systems.
- The collaborators are a strength of this project.
- Strengths of the project include the scope of collaboration and the detailed model.
- This is a useful tool for evaluating a potential installation.
- A key project strength is that the tool is developed in open-source software.
- This is really cool, versatile, widely applicable, user-friendly software.

Project weaknesses:

- This reviewer admits to being confused by this project, and this is reflected in the reviewer’s scores. The DOE goal as stated on slide 3 is to develop medium-scale CHP fuel cell systems that achieve 50% electrical efficiency, 90% CHP efficiency, and 80,000 hours of durability at a cost of $1,500/kW for operation on natural gas, and $2,100/kW for operation on biogas by 2020. It is not clear how the development of the DG-BEAT tool helps to achieve that goal. The PI needs to explain this in much more detail. This could be a poor selection of the DOE goal being addressed. If the goal is to support implementation of CHP systems in the marketplace, then this model would be quite useful. However, that is not what the selected DOE goal states.
- Quality control of the different modules has to be validated. The proposed designing and cost optimization have not been validated through existing installed fuel cell systems.
- More could be done to make the model available to others and to increase the amount of validation it receives.
- The role of collaborators and the value added by collaborations was not clear. There seems to be limited effort to address model uncertainty and the information value of model design choices.
- The planning for model validation is not clear. Priorities were not clearly identified for 2014 or future work.
- Quality control of the different modules is still ongoing. Validation procedures need to be developed for assessing the fidelity of the model and the data.
- The work does not seem to have been adopted yet by manufacturers—this has to be accomplished.

Recommendations for additions/deletions to project scope:

- Addressing quality control and quality assurance is important. The ability to value (in dollars) the avoided emissions would be a useful addition to the model. The researchers noted that they will be engaging in a model validation. This type of model should be the subject of an ongoing performance evaluation. More realistic assessment of what emissions are offset would be a useful but challenging addition to the model—this is something that should be done in collaboration with other laboratories.

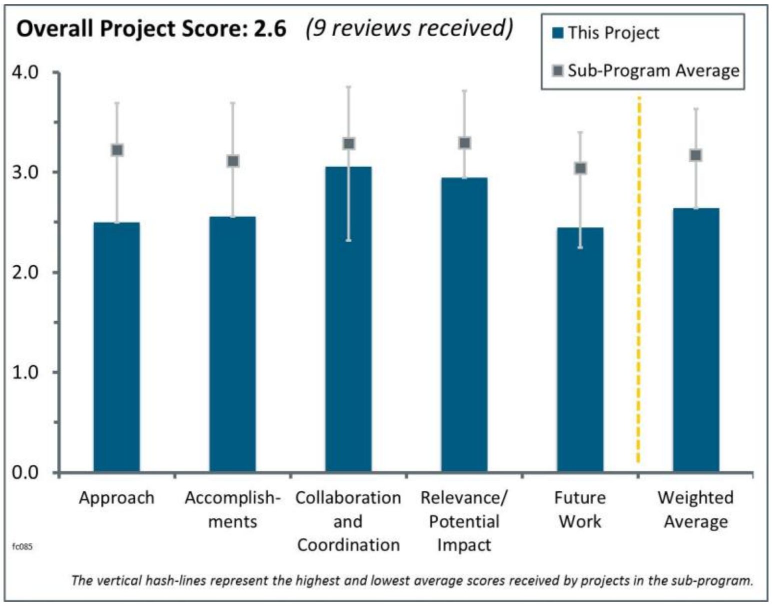
- The team should focus more on mainstream validation testing of the model; it should engage the User's Group for this purpose. It should also decrease efforts on new blocks that still present high uncertainty, such as emissions, unless specifically requested by the model customers.
- The team should present a validation of the model from experimental data.
- The researchers should revisit and adjust the DOE goals and the project goals to bring them into alignment.

Project # FC-085: Synthesis and Characterization of Mixed-Conducting Corrosion-Resistant Oxide Supports

Vijay Ramani; Illinois Institute of Technology

Brief Summary of Project:

Research objectives in this project are to: (1) develop and optimize non-carbon support materials with high corrosion resistance, high surface area, and high electron conductivity; and (2) develop cathode catalysts consisting of Pt deposited on the novel non-carbon supports, and determine the performance and durability of these supported catalysts in in situ and ex situ testing. This project also will develop a cost model for the optimized support materials.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **2.5** for its approach.

- The approach has been narrowed to focus on the most promising high-performance supports: RuO_2-TiO_2 (RTO) and indium tin oxide (ITO). The team has done very well in meeting the desired support properties and milestones for these materials. However, there are still critical catalyst performance obstacles to overcome, as well as a severe issue with ITO performance in membrane electrode assemblies (MEAs) that needs to be identified and resolved.
- Investigation of oxides as replacements for carbon as fuel cell support materials has merit. The shifts in the project to decrease the amount of Ru used by further supporting it on TiO_2 and to investigate ITO both make sense from a cost consideration standpoint. The investigation of oxide supports has seen reasonable efforts to date, and while the choice of materials investigated has some rational basis, it is not overly compelling.
- The approach is well justified by utilization of both rotating disk electrode (RDE) and MEA in evaluation tests for different oxide material supports for the Pt catalyst.
- It is certainly necessary to explore oxides as support for the oxygen reduction reaction (ORR) catalysts. The selection of oxides could have been different had the researchers considered some experience from other uses of the selected materials. For example, in chlorine production it is known that RuO_2TiO_2 mixed oxides are excellent electrodes for Cl_2 evolution, but that the surface dissolves in O_2 evolution at potentials above 1.4 V. RuO_2 is not stable in the ORR, while SnO_2 is not stable in Nafion®.
- The approach is to replace carbon supports with metal oxides functionalized with proton conduction to eliminate issues with carbon corrosion. The metal oxides explored seem to be primarily SnO_2 and ITO; previously RuO_2-SiO_x and combinations of these were explored. Comments were made that SiO_2 and SnO_2 are chemically stable; previous fuel cell results would indicate that this is not really true. Sn included as an alloy agent in Pt dissolved out (work from Professor Ross [Berkeley]), SiO_x has been problematic over the years in regard to Si gaskets, and SiO_x fibers in microporous layers have shown Si migration all over the cell. The potential cycling approach follows relatively standard methods; however, in these cases, exposure to the oxidizing and reducing atmospheres needs to be included.
- The approach of using oxides to improve corrosion resistance is challenging because these oxides have low conductivity. The project is meeting milestones for improved conductivity but the performance of the MEAs is still far short of U.S. Department of Energy (DOE) targets. The corrosion resistance and stability shows improvement over the reference Pt/C catalyst.

- The project looks at mixed metal oxides as Pt supports. The Pt/ITO catalysts are evaluated using durability protocols that are divergent from the DOE protocols. It is important to compare the DOE and Nissan protocols with state-of-the-art Pt/C catalysts to understand their differences. The Pt/ITO catalyst durability seems to be compared to Pt supported on high surface area carbon (HSAC) support, which does not exhibit good corrosion resistance. A comparison with a corrosion-resistive graphitized C support would be valuable.
- This project continues to rely on supports with questionable stability (ITO in particular) and generally unimpressive conductivity. The approach is generally not innovative. Ruthenium oxide (or mixed oxides) is a no-go not only because of the likely prohibitive cost, but also because of the strongly inhibitive effect of Ru on the ORR.
- The approach of using Ru and ITO for Pt support is not based on fundamentals—thus, it has resulted in poor results.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.6** for its accomplishments and progress.

- The project team has made excellent progress toward meeting the milestones and scaling up the synthesis of the catalysts.
- Better performance and durability were achieved for the Pt/RTO system versus other supports. However, the total cost that includes durability and performance is still higher for Pt/RTO than for Pt/C.
- The progress over the last year is good. It is confusing that the MEA performance is so poor. Literature suggests that the ITO hydrolyzes and causes structural deformation. It is important to understand whether the increased Ohmic resistance is the only contributor to the poor MEA performance. Thus, it may be worthwhile to conduct analyses of the different voltage loss mechanisms of the MEA and the structural changes of the catalyst layer structure with aging (changes in porosity, limiting current). Furthermore, it is important to understand the interaction between ITO and the ionomer. X-ray photoelectron spectroscopic (XPS) measurements of as-prepared, conditioned, and aged catalyst layers would provide information on the changes in surface speciation with operation.
- Syntheses of oxides and deposition of Pt are apparently successful. However, Pt loadings of 44 µg /cm^2 are prohibitively high. It would be better to use 10–15 µg /cm^2. All deficiencies would have been observed within a short time. Information on the oxide-Pt interaction also depends on loading. Therefore, the data for the loading that cannot be used is not helpful. It is not difficult to obtain high activity with that loading. The cost analysis is also affected by a large loading.
- The technical accomplishments are relatively minor in terms of advancing the technology in the target area of improved performance and durability. A number of new materials were synthesized and screened, but the project has not advanced the science of these materials in a meaningful way. Down-selecting to the materials studied is sensible, but the materials set that was investigated is still quite disconnected in terms of characteristics and properties, requiring a broad focus rather than detailed investigations of fundamental limitations that could be used to overcome shortcomings for a single materials set. There has been a general lack of surface science applied to these studies to determine what key variables dictate performance and durability. The Transmission electron microscopy (TEM) shows small Pt particles (3–4 nm), but Pt surface areas have been limited to ~20 m^2/g Pt in almost every case. At this ECA, it is highly unlikely that these materials could ever exhibit sufficient mass activity, even at beginning of life, regardless of durability. The differences between RDE and MEA are interesting, but it is unclear whether it is possible to understand or resolve them.
- Accomplishments for fiscal year (FY) 2014 are mostly related to making ITO and supporting Pt on ITO. A number of materials were synthesized and characterized, mass activity was measured, catalysts were subjected to accelerated stress tests (ASTs), and MEAs were fabricated and tested. Pt electrochemical surface area (ECSA) is low (by ~4x) compared with traditional Pt/C-supported catalysts. Pt/ITO was evaluated for ECSA decrease during AST measurements, and was nearly identical to that of Pt/C in terms of percentage of ECSA loss. The MEA performance is very low, showing poor kinetic performance, high resistance, and what could also be mass transport limitations.

- The team has dedicated significant effort toward developing and testing the new ITO supports. Unfortunately, several obstacles remain—most importantly, the poor performance in MEA. While the team had some good insight into the cause of the poor performance (formation of hydroxide species due to hydrolysis of the ITO surfaces), it did not propose any possible solutions or paths forward. Good progress has been made in controlling particle size and dispersion on ITO and RTO, and it is exciting to see both the reproducible synthesis with scale-up and retained ECSA and mass activity upon Pt loading reduction. Going forward, greater attention needs to be placed on understanding catalyst-support interactions and their impact on performance if ECSA and mass activity are to be improved.
- This project is in its fourth year, and so far it has not generated materials that would be remotely viable for polymer electrolyte fuel cells. There is very little fuel cell performance testing in this presentation; the results shown (slides 17 and 26) attest to very low activity of the Pt catalyst, even on O_2. ESCA is very low for all ITO-supported catalysts. At present, there seems to be no path toward bringing the mass activity of the catalysts to the level required.
- All of the catalysts shown here have low ECSA and mass activity compared to baseline Pt/C; having a durable but really poor activity is a nonstarter. This project is not a good investment of DOE funding—it is unclear how the project made the go/no-go gate.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- The collaboration with Nissan is apparently excellent, involving experts in the fuel cell electrocatalysis.
- The collaboration between Nissan and the Illinois Institute of Technology (IIT) appears to be working well, although this is a limited set of partners.
- The partnership with Nissan provides the ability to test the materials under real-world conditions. There is close cooperation between Nissan and the IIT team.
- The collaboration with the Nissan Technical Center North America (NTCNA) has gone very well. It is great to see that NTCNA housed a student this year. It was not clear why the ITO mass activities measured by NTCNA (150 mA/mg) were so much higher than those reported by IIT for the various synthesis protocols.
- Input from all participants in the project is evident from the slides, and the work was well executed and supports the overall project goals.
- The collaboration with Nissan seems to be effective and working well.
- The project has a reasonable team working together.
- The project only involves two institutions—IIT and Nissan. The involvement of other institutions (perhaps even as in-kind contributors) would be very beneficial. Catalyst suppliers or other research projects have developed catalysts based on oxide supports (e.g., Pt/SnO_2 from Tanaka Kikinzoku Kogyo (TKK) and TiO_x at Los Alamos National Laboratory), and using these materials as baseline comparisons in testing could provide useful comparisons (the table on slide 9 was useful, but a broader materials set with specific values filled in would have increased its value). Additionally, organizations that could offer surface science techniques (particularly in situ techniques) or modeling studies to help understand degradation processes would be useful.
- Collaboration is limited to only two partner organizations: IIT and Nissan. No other entities appear to be involved.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.9** for its relevance/potential impact.

- Information on the stability of some oxides in MEAs and their usefulness as Pt support is useful background knowledge.
- The project addresses the corrosion of the carbon supports—one of the key aspects of fuel cell durability with cell start-up/shutdown operation.

- The supports developed under this project have the potential to greatly improve stack durability.
- This project is relevant to DOE Hydrogen and Fuel Cells Program goals, but its impact has been insignificant to date.
- More durable supports would help the project team achieve the performance and durability targets related to the degradation of carbon supports. However, for this impact to be achieved, the material performance needs to be competitive in terms of mass activity.
- Improving the durability of supports would allow less stringent engineering approaches to be put in place to avoid the issue of carbon corrosion that limits current materials in fuel cell systems. The materials developed also need to meet all system requirements (e.g., mass activity and Pt dissolution).
- The project is well aligned, but it has significant technical hurdles to overcome.
- Increasing the stability of supports for Pt catalysts is a critical barrier to the implementation of fuel cell technology. This project offered promising alternatives to traditional carbon based supports that, to date, remain uncompetitive. However, new directions for further research have been identified.
- This project is not solving any of the key challenges highlighted by the Fuel Cell Technologies Office. Even though the project team claims that it is solving the durability aspect, low degradation is not valuable if the catalyst activity is very low.

Question 5: Proposed future work

This project was rated **2.4** for its proposed future work.

- Considering that this is the final year of the project, the scope of the proposed work is appropriate. If completed, it will answer outstanding important questions and initiate technology development.
- The future work outline is adequate. It is important to understand the cause of the poor MEA performance of the ITO catalyst. Work on reducing the ionomer concentration with ITO-based catalysts only makes sense once the poor MEA performance is understood and mitigated.
- The success of the ITO depends on whether the MEA performance issue can be resolved, so clearly this is an essential part of the future work. The path forward for the RTO support was not as clearly established. An effort dedicated to understanding microstructural changes to the catalyst and support in MEA should be strongly considered.
- The addition of XPS studies and the investigation of the difference between RDE and MEA studies are both very sensible. With the little time and funding left for the project and the quality of materials generated to date, it does not make sense to pursue scale-up and large cell studies or Nafion content optimization. It is best to stay focused on a single material set and try to get some fundamental understanding of the system.
- According to the FY 2013 Future Work section, several of the work items listed in this year's Future Work section were supposed to be finished by now—specifically, the ITO supports and the cost model. It is unclear if there is a reason these were not completed as stated in FY 2013. It was probably required in the funding opportunity announcement to make large-scale MEAs, but seeing that the mass activities of Pt/ITO etc. are not comparable to Pt/C (close to Pt/graphitized carbon) and do not come very close to the DOE mass activity targets, it seems that the priority should remain developing high-mass-activity catalysts rather than scaling the MEAs. Additionally, the MEA results were poor, so improving the MEA performance is required, but not needed to scale.
- Reasons for the disappointing performance of ITO-supported catalysts in the MEA should have been addressed much earlier in the project. They are almost certainly related to Sn leaching (and possibly the instability of In, as well). Cost modeling and MEA fabrication scale-up are out of place as long as supports are not stabilized. In the time remaining, the research effort in this project should concentrate on the development of new support formulations.
- To complete this study, the researchers have to complete the initial plan, but they should also test 15 µg /cm^2 or less.
- The project needs to focus on improving the specific activity. The Pt loading is still very high compared to the reference catalyst.

Project strengths:

- The collaboration between academic and industrial partners was strategically executed and has led to valuable feedback on the utilization of metal oxide materials as feasible alternatives to carbon supports. Notable progress was achieved in support durability.
- The project has looked at several different materials and processing conditions. There is a reasonable premise for the materials chosen for investigation.
- The interaction between IIT and Nissan is very strong and well-focused. The team has been very successful in producing durable supports.
- The project features a good team of experts and good collaboration.
- The corrosion stability of these supports is the major strength of this project.
- The strength of the project is the good/clear presentation.
- Investment in alternative supports is needed and should continue.

Project weaknesses:

- Besides the obvious MEA performance issue, more attention needs to be given to the morphology and interaction of the particles and support in order to make further headway on improving activity and reducing Pt loading. It would be very useful to study the catalyst morphology after testing to further validate the durability results.
- The stability of these support materials in the fuel cell environment needs to be demonstrated, including at potentials from 0 for 1.0 V, and with exposure to O_2 and hydrogen. These are exposed not only to acidic media, but also to varying potentials and both oxidizing and reducing atmospheres.
- Weaknesses of the project are the relatively limited team and the lack of specific understanding of degradation mechanisms and fundamental materials limitations.
- Even though performance is satisfactory, the total cost analysis does not indicate a path forward for implementing the results in technology.
- To date, this project has not provided any materials of potential value to polymer electrolyte membrane fuel cell technology.
- Selected oxides are not stable under Nafion; Pt loadings are too high.
- The low ECSA is a major weakness.
- This project features the wrong fundamentals.

Recommendations for additions/deletions to project scope:

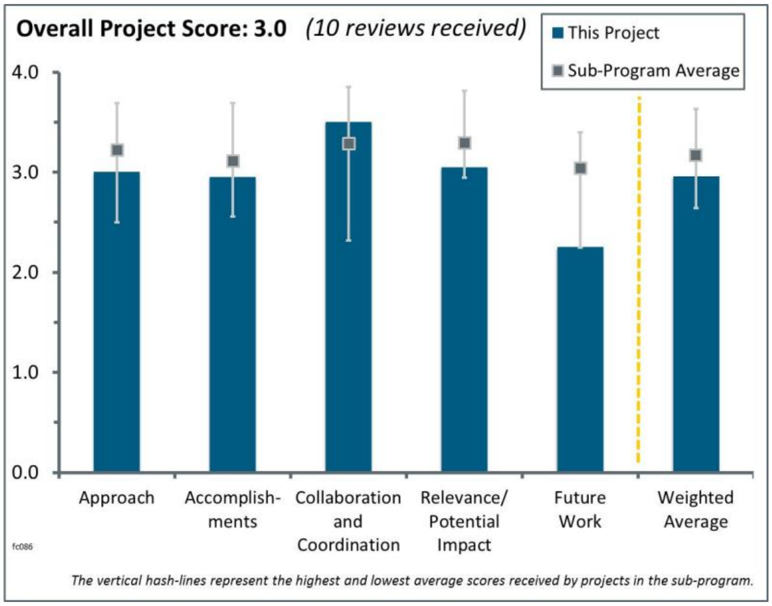
- The project needs to focus on alternate methods for deposition of Pt to achieve higher mass activity. The researchers should determine if the lower performance could be caused, in part, by the alloying of Pt with the support.
- Due to the instability intrinsic to the chemical formulation of ITO and the well-established detrimental effect of Ru on the ORR, both supports need to be abandoned and new formulations need to be developed.
- Researchers should limit efforts to ITO with an increased focus on surface studies—this is in line with the proposed future work. The team should not pursue scale-up of materials or large-cell MEA studies.
- The researchers should develop a fundamental understanding of the interaction between the metal oxide support and the ionomer.
- This project should concentrate on improving the Pt mass activity and increasing the Pt ECSA. Otherwise, the MEA design and performance, and especially scaling, is irrelevant.
- The team should select the low-coverage oxides for further study.

Project # FC-086: Development of Novel Non-Platinum-Group-Metal Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

Sanjeev Mukerjee; Northeastern University

Brief Summary of Project:

This project will develop new classes of non-platinum-group-metal (PGM) electrocatalysts to meet or exceed U.S. Department of Energy (DOE) targets for activity and durability. The approach includes: (1) development of novel reaction centers for oxygen reduction, (2) controlled metal support interactions for efficient mass transport of charged and solute species, (3) control of the electronic structure of reaction centers, (4) computing transport and reaction dynamics, and (5) spectroscopy to elucidate electrocatalytic pathways in complex reaction centers and quantify degradation with element specificity under in situ operating conditions.



Question 1: Approach to performing the work

This project was rated **3.0** for its approach.

- The team has developed a multifaceted approach for the synthesis of non-PGM electrocatalysts. The researchers have demonstrated scale-up of their catalysts. The approach involves modifications of the catalyst at both the nanoscale and the mesoscale to address intrinsic activity as well as transport issues. This is key to the success of this team.
- The approach is well thought out and takes into account multiple barriers that need to be addressed in order to develop active and durable non-PGM catalysts.
- The approach has been adequate for the magnitude of progress that must be made to achieve success. It is not adequate for the last year of the project, with so much distance still to cover.
- The elements within the project approach are all good, but they are huge in scope if they are to be as effective as implied by the relevance and impact statements. The targets for evaluating the success of the catalysts, based on volumetric current density, are not sufficient for effective screening and determining go/no-go for automotive applications. If the project proposes to be as effective as implied by the relevance and impact statements, then the catalysts should be evaluated in the same way as PGM catalysts, both from performance and durability standpoints. This does not mean that a low-current-density performance would automatically be declared a failure. What is important is that the actual gap between the current performance and where it has to be to be realistically effective is made clear. This will allow better judgment of what is critical to be worked on, whether it is fundamentally possible to overcome the gaps, whether it is worthwhile. Finally, it is not clear why this approach will still not be subject to the fatal flaw of carbon corrosion at cycling potentials up to 1.5 V as expected in starting/stopping.
- The project uses a solid approach combining advanced synthesis, state-of-the art analytical tools, and molecular modeling to make significant improvements to non-PGM catalyst performance. The researchers have also appropriately focused on high-current-density performance in air. The biggest flaw in this approach is the use of Fe in the catalysts, which can accelerate membrane degradation if it leaches from the catalyst. It is strongly recommend that the team eliminate Fenton’s active transition metals.
- The technical approach is comprehensive and seems reasonable to achieve the goals of the project. Because it is now well established that in addition to the low activity, durability is a serious issue, all samples should be screened for corrosion by using a simple test by rotating disk electrode (RDE) where the catalyst is

subject to a sweep from 0.0 V to 1.8 V in acid and the onset of corrosion currents are compared to that of Pt/Ketjen Black and/or Ketjen Black. This might save a lot of time before activity studies are started. Activity data should include the catalyst layer resistance obtained from electrochemical impedance spectroscopy (EIS) over a range of frequencies under N_2. This will provide a measure of the thickness of the catalyst layer, which is a serious problem and has been bypassed by using an areal activity instead of volumetric activity. If the catalyst layer is too thick, it will have high resistance and high O_2 diffusion overpotentials. Also, the stack components will increase in number or size, leading to a high stack cost even if the catalyst has zero cost.

- The approach includes several classes of non-PGM catalysts from the various partners. Screenings were performed with O_2 RRDE measurements with peroxide selectivity measurements included, at least for some of the catalysts presented. The durability testing by Nissan is also very interesting. The non-PGM catalysts tested do well in load cycling, but understandably poorer in start-stop testing. Power plants that employ known voltage management techniques during start-stop may enable these catalysts. However, it would be interesting to do some microstructural characterization of the accelerated-tested catalysts to see if they maintain their structure. The approach could be augmented with more diagnostic performance testing with varying O_2 contents and helox in order to better calibrate the Michigan State University (MSU) modeling. Also, more microstructural characterization of the fabricated electrodes would be helpful. It is not readily apparent why catalysts that achieve the 2010 volumetric current density target still struggle so much in membrane electrode assembly (MEA) testing using 2.5 bar, fully humidified air. It seems that the C and ionomer ratios make a big difference, so more focus here may yield better-performing electrodes. Perhaps adding hydrophobic constituents may improve the porosity and flooding tendencies.
- The project has shown useful results using relevant tools and includes some materials of promise for the development of non-PGM catalysts, but the vision of the overall approach was not clearly conveyed in a way that leads to a high degree of confidence in the rationale of the materials set being investigated. More specifically, slide 6 shows four distinct approaches for Tasks 1.1–1.2, but the three approaches presented in slide 7 do not specifically map to those in slide 6, and it is unclear how they are connected, what synergies they have, or how decisions have been made on choices for topical areas/approaches of focus within the material development effort.
- The emphasis on scale-up (at Pajarito Powder, LLC [PPC]) of materials with readily measurable kinetic activity and high-current-density performance is something the non-Pt field really needs and should significantly advance the field by allowing the start of detailed mechanistic studies. This project originally planned too wide a range of approaches, some of which are dubious but probably sounded good to some reviewers of the original proposal (e.g., biomimetic oxygen reduction reaction [ORR] catalysts—standard FeNC non-Pt ORR catalysts started off biomimetic, but needed to diverge significantly from hemoglobin to obtain half-decent activity and durability under realistic fuel cell conditions), but the project seems to be settling down to a more-restricted set of reasonable activities. The high-current-density target of 1 A/cm^2 at 0.4 V would be useless in practical application due to low efficiency and excessive heat generation. It needs to be stressed that this “target” is just a starting point needed to get the work off the ground. The target for transportation applications, the highest-value market for fuel cells, would likely be at 0.7 V or higher. Because these are C-based catalysts, they should not be expected to provide a materials solution to start-stop (i.e., the team should not spend a lot of time testing cycling 1.0–1.5 V). Such catalysts would clearly require systems mitigation of these issues, which should be possible.
- Although the results obtained are very good, or excellent, the approach of involving a number of dissimilar molecules, treated in a variety of ways (e.g., ball milling, pyrolysis, metal-organic framework [MOF], and blending) looks like a trial-and-error procedure. A more coherent choice of molecules, supported by an underlining theory, would allow for more-efficient research.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.0** for its accomplishments and progress.

- The progress toward demonstrating the DOE non-PGM targets and understanding possible mechanisms has been impressive. But when the accomplishments are looked at in terms of whether they (the accomplishments) help overcome the larger barriers to automotive fuel cells, they are only modest at best. Automotive applications require cell potentials above 0.6 V, and these current densities under air are an order of magnitude too low. An attempt should be made to project the highest possible reduction potential and site density to estimate the highest possible current density such a non-PGM system could give and see if an order of magnitude improvement is possible. Also, the cathode non-PGM catalysts should be evaluated in MEAs that have Pt anode loadings consistent with, or slightly higher than, what PGM cathodes are required to use in order to hit the 0.125 mg/cm^2 of total PGM targets. The high anode loadings used to evaluate these non-PGM cathodes can skew the results. Also, as higher-voltage cycling or stop-start cycling is done to more realistically evaluate the non-PGM cathode stability (e.g., to 1.5 V), Pt dissolution from the anode and diffusion to the cathode will occur and further confuse and skew the results.

- The researchers made excellent progress last year, in particular regarding catalyst activity. Catalyst stability, however, remains a major problem, further aggravated by the H_2O_2 observed. The understanding of the behavior of these catalysts is far from complete—in particular, the role of the Fe_2+/Fe_3+ redox couple in determining the open-circuit potential. It appears that a mixed potential is operative. If one process is corrosive in nature, that is not good news for stability. It remained unclear why CN- adsorption causes only a partial blocking of active surface, even at its high concentration in the solution phase.
- The project has done an excellent job achieving the very challenging targets for hydrogen/air fuel cell performance. The principal investigator (PI) recognizes that there is still a long way to go and has ideas to hopefully bridge the gap to meet the ultimate automotive targets. It is still a longshot to meet these ultimate targets, but the potential benefit is worth the effort.
- These non-PGM catalysts have come a long way from where they have started. However, they are still a ways away from being practical replacements for PGM on cathodes. The problems do not seem to lie in the fundamental ORR kinetics. The mechanistic studies are interesting, but it is not clear how these insights are leveraged toward other potential non-PGM catalyst formulations.
- Very good progress has been made toward achieving the DOE activity targets at 0.8 V, both in O_2 and air. The high-performance target (at 1 A/cm^2) has not been achieved. The researchers have made significant progress toward revealing the mechanisms of the ORRs on non-PGM catalysts, as well as excellent progress with catalyst scale-up.
- The team has made significant progress on multiple fronts. The researchers have synthesized large batches of catalysts, and they have also investigated the durability of these catalysts. These catalysts, along with conventional Pt catalysts, do not appear to survive during start-stop cycling.
- Reasonable performance and results have been obtained with a number of materials. The mechanistic studies and spectroscopy results are by far the most interesting. Unfortunately, the PI left little time for detailed discussion regarding the mechanism and active site; instead, the PI spent too much time on less interesting topics such as background introduction and scale-up, which could have been handled much quicker. From just the slides and question-and-answer (Q&A) session, the validity of the proposed mechanism and active site findings is harder to judge, but even the inclusion of such a mechanism with some supporting data is useful to the field.
- Meaningful progress has been made in generating non-PGM cathodes that give measurable performance at high current density. The team has also made good progress on scale-up, which can be a very difficult problem with this class of catalysts. A start has been made on mechanistic interpretation, with a claim that two types of sites are needed in acid. The conclusion that ORR activity correlates with the potential of the Fe II–III couple for FeNC systems seems inconsistent with some reliable data in the literature. Active catalysts of this class often do not show any discernable Fe II–III couple when cycled in inert-purged acid.
- It is clear that some elements of progress have been demonstrated, but much remains to be done in order to achieve targets.
- There are no slide numbers on the slides themselves. Slide 13 has DOE standard conditions (0.5 bar O_2?) on the figure, which are questionable. It looks like the slides were made by different people and were not checked carefully by the PI. It would be good if Pt/C data was superimposed on all ORR I–V plots for comparison under the same conditions. It is difficult to judge the results without it. Slide 16 has units of pressure as bar-g! Units should always be the International Standard of Units (SI), which are absolute units and do not have gauge pressure, such as 100 kPa. (Otherwise, the ambient pressure in Nm needs to be known and reported.)

Question 3: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- The project involves multiple institutions that are all contributing to the project. The collaboration among the team members is excellent, leading to a synergistic research effort.
- There appears to be a strong collaboration among the team that includes academic, industrial, and national laboratory partners.
- The project's collaboration involves several leading specialists in this area of electrocatalysis, one catalyst producing company, and one car manufacturer. It is well structured and coordinated.
- A good mix of academia, suppliers, national laboratories, and original equipment manufacturers (OEMs) are involved.
- The team members are very strong leaders in the fields of electrochemistry, spectroscopy, and non-precious catalysis.
- This is a very well-coordinated effort between academia and industry.
- The collaboration seems sufficient, especially for scale-up.
- This appears adequate thus far.
- This is a complex project, but it seems to leverage the strengths of the partners particularly well. There is good focus on scale-up of the catalysts by PPC. One will need to see more impact by Nissan toward the end of the project in testing larger-scale MEAs in cells and stacks.
- Collaborations generally seem to be working well. They are a bit heavy on academia and small spinoffs. Interactions with the non-funded collaborator, Canetiq, should be explained. The role of theory within this project seems a bit unclear from the presentation. It appears that MSU's modeling of electrode layer performance needs to be better integrated into the project as a whole, if it is to continue.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.1** for its relevance/potential impact.

- If durability issues at start-stop cycles and performance targets at 1 A/cm^2 are achieved, the project has the potential to significantly advance progress toward commercialization of polymer electrolyte membrane fuel cells (PEMFCs).
- Developing non-PGM catalysts is very important for broader application of fuel cell catalysts.
- The removal of PGM from fuel cell cathodes would be a major development toward the cost and supply viability of automotive fuel cells. While more progress is needed, this project has made some impressive strides.
- Development of these catalysts will take some time, and the potential impact could be delayed.
- This is a more exploratory effort in the DOE Hydrogen and Fuel Cells Program, but it is aligned.
- There is an obvious benefit to eliminating PGM from the electrode. This is a high-risk, high-reward project.
- This project addresses the holy grail of ORR research: non-noble-metal catalysts with adequate activity, performance, durability, and robustness. A high-current-density target of 0.4 V at 1.0 A/cm^2 is way too low for practical application and does not fulfill the quoted "Relevance to DOE Mission" on slide 3: "This will enable decoupling PEM technology from Pt resource availability..." It is, however, a realistic goal within the original time frame of this project. This project, and others, has made substantial improvements to the engineering status of non-PGM catalysts, but very substantial reengineering of fuel cell systems would still be required to allow use of such radically different catalysts in practical applications, even if all project goals are met. Success of this and other DOE Office of Energy Efficiency and Renewable Energy non-Pt catalyst projects could facilitate the start of serious work to address durability and robustness issues with non-PGM catalysts.
- Non-precious-metal catalysis has made meaningful progress toward improved performance and durability, but they remain far below the levels required for MEA transportation targets. With improvements in Pt-based catalysts resulting in the potential to achieve ultra-low loadings in vehicles, the cost driver to replace Pt is greatly reduced, meaning that non-PGM materials will have to essentially be equal to Pt-based systems; this is an unlikely advance, even with the significant advances that have been made to date.

- Because of their low activity and durability, non-Pt catalysts have a long way to go before they can be considered useful for automotive PEMFCs; however, they need to be worked on for the next 10 years or so. At some point, there should be a clear break in funding if it is realized that non-Pt catalysts will never be stable enough for load cycling durability or if the Pt loading is low enough (10 g/100 kW) that the Pt cost is not a concern and, with recycling, is not an issue anymore. It is a bit confusing and disconcerting that the targets for activity are reported in different ways in different slides, with incomplete information on temperature, P_{O2}, etc. The targets are being changed from volumetric to areal units, but it should be clearer and well defined. RDE targets/benchmarks do not exist and need to be established for screening catalysts at a rapid rate.
- The relevance and impact seem to be highly overstated. If the project meets all of its objectives, it would not accomplish the things stated in the relevance and impact sentences. These sentences seem to be generic relevance and impact statements used by DOE to justify working on non-PGM catalysts. However, in order for the catalyst materials to overcome those automotive barriers, they will have to meet all of the much more rigorous performance and durability tests that PGM catalysts have to go through, which are outside the scope of this more basic research effort.

Question 5: Proposed future work

This project was rated **2.3** for its proposed future work.

- The future work is well directed, but it needs to focus on better definition of active sites and methods to increase active site density. It is not clear if the large Fe nanoparticles play any role in the catalyst performance.
- There was no future work slide. The presentation by the PI was professorial—it was similar to a university lecture, and he did not finish his talk and go through all the slides, because he got caught up in long discussions about the work, but not on the work. It would be nice if this changes—it is becoming a tradition. There are far too many technical slides presented together in a rush, and it is hard to figure out the accomplishments and future work.
- No future work slide was provided. From the plan, it seems like stack testing is part of the future work. Catalyst scale-up and stack testing is premature at this point. Significant performance gains are still required beyond the project’s high-current-density target. Rather, the project should focus on finding ways to increase the active site density and developing active catalysts that do not contain Fe.
- The future work is not clearly laid out, just the completed percentage of milestones provided toward the beginning. Therefore, it is not clear exactly what steps will be taken to address the high-performance-target gaps. The project may be trying to do too much—it seems like a focused project will either focus on structure-function determinations of novel catalysts for the ORR, or attempt to optimize the down-selected University of New Mexico catalyst. This reviewer would vote for the latter. If the high-performance gap can be significantly bridged, then these catalysts may be taken more seriously by OEMs.
- The presentation lacked the mandatory future work slide, and due to time management the speaker rushed through the slides at the end of the presentation. Based on comments made throughout the presentation and the Q&A session and the approach demonstrated by the team to date, it is expected that the future studies will have some relevance; however, the lack of a future work or remaining barriers slide is a major oversight by the PI.
- The proposed future work is not described, but it is linked to the milestones and go/no-go decisions. Modeling, density functional theory calculations, and increased spectroscopic characterization will provide a new quality to the data.
- The efforts required to achieve targets in this final year are quite large, and the plans to achieve them were not documented and explored.
- No future work is provided. Quarterly milestones that are related to future work identify only milestones, but not the path to accomplish these milestones.
- Unpyrolized MOFs seem to be a big divergence from what has been productive in the past. More attention could be given to the development of methods to quantify the volumetric density of active sites.
- There were no slides addressing future work.

Project strengths:

- This project features a notable mix of synthesis, performance evaluation, and characterization. It also features scale up of catalyst preparation to levels that could enable detailed mechanistic, durability, and robustness testing.
- Project strengths include the rich set of non-PGM approaches, the focus on scale-up, and the characterization of fundamental ORR activity.
- Strengths of this project include its good mechanistic studies and presentation of a plausible ORR mechanism with supporting data.
- The project features good collaboration within a strong team. In addition, a broad range of characterization techniques are used.
- Using advanced characterization techniques and modeling allows for fast progress toward revealing reaction mechanisms and identifying reaction active centers.
- The researchers have developed novel approaches for the synthesis of non-PGM catalysts and demonstrated performance that successfully passed the go/no-go benchmarks.
- The PI has assembled a strong team that is using a sound approach to address the most challenging aspect of non-PGM electrodes—high-current-density performance in air.
- Strengths of the project are the clever PI and the good set of collaborators.
- This project has a good approach.

Project weaknesses:

- There is no clear path to achieve the performance target at 1 A/cm^2. Iron nanoparticles even surrounded by carbon shell might cause durability issues due to Fe dissolution in a strongly acidic environment and generating peroxide radicals. Peroxide generation has to be reported not only as a ring current, but also as H_2O_2 yield on slide 22.
- The voltage target for high current density in air is too low to ensure any practical utility. The project needs more emphasis on the durability of high-current-density performance in air at practical operating voltages (above 0.6–0.7 V).
- No clear direction was presented regarding a hypothesis for further improving performance/durability, nor were there clearly planned steps. There is a lack of clarity regarding future direction.
- The catalyst is quite heterogeneous and contains multiple sites and functionalities. The lack of a definition of the active site may hamper future efforts at improving the catalysts.
- The slides need work, as do the benchmark values reported and the general comparison to a solid baseline ORR curve.
- Project weaknesses include the basic limitations of non-PGM materials and their poorly understood site densities and ORR turnover mechanisms.
- There is a lack of coherence in the systems selected for detailed studies.
- One weakness is the apparent dependence on Fe for high ORR activity.
- The project needs more fundamental work on electrode optimization.

Recommendations for additions/deletions to project scope:

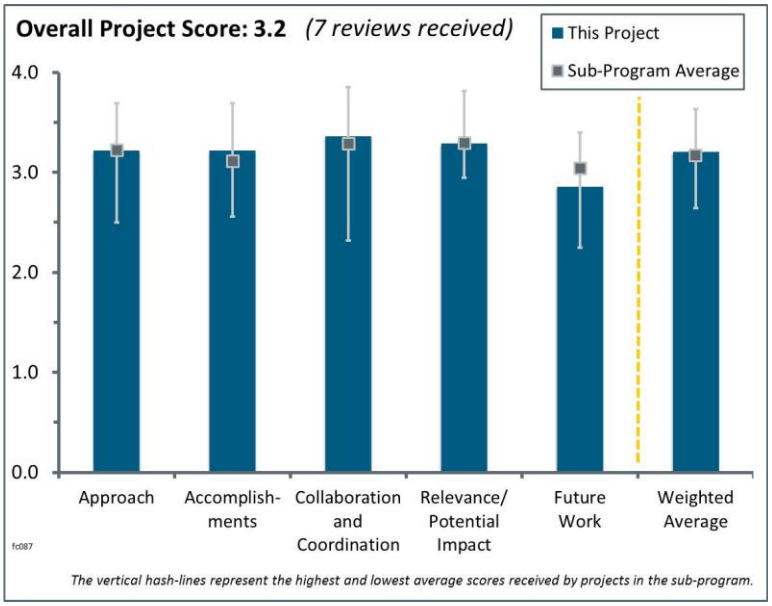
- The researchers should make the targets more rigorous and consistent with the PGM catalyst approaches, because it is the application that is important, not the explicit approach to get there. Therefore, they should incorporate high-voltage cycling tests to address the potentially fatal flaw of carbon corrosion at 1.5 V. They should also add a goal to determine the maximum projected activity capable with this catalyst approach based on realistic estimates of redox potential limits and site densities per unit volume, and then see if it is even remotely possible to get where PGM catalysts are today.
- The team should add an explicit attempt to quantify the concentration active sites in the catalyst layer (this is admittedly very difficult). It should also actively coordinate with the more recently initiated Los Alamos National Laboratory non-PGM catalyst project to rationally divide up tasks. It should be careful not to expend too much time on non-pyrolyzed catalysts with inadequate performance and durability.
- The team should increase the understanding of the behavior of Fe_2+/Fe_3+ and the role of H_2O_2 in stability. Partial inhibition by CN- offers additional information on active sites.

- The PI should move away from Fe-containing catalyst systems that are likely to accelerate membrane chemical degradation.
- Durability tests should be conducted at 0.05 mgPt/cm^2 loading at the anode.
- The project team should conduct further characterization of the active sites and site density.

Project # FC-087: High-Activity Dealloyed Catalysts

Anusorn Kongkanand; General Motors

Brief Summary of Project:



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

The goal of this project is to reduce catalyst cost while achieving the required durable performance. The objectives of this project include: (1) demonstrating reliable oxygen reduction reaction kinetic mass activities greater than the U.S. Department of Energy (DOE) target in hydrogen/oxygen fuel cells; (2) using manufacturable synthesis and dealloying procedures; (3) achieving high-current-density performance in hydrogen/air fuel cells adequate to meet DOE heat rejection targets and Pt-loading goals; (4) demonstrating the durability of the kinetic mass activity against DOE-specified voltage cycling tests in fuel cells; (5) determining where alloying-element atoms should reside with respect to the catalyst-particle surface for durable activity; (6) demonstrating the durability of high-current-density performance; and (7) scaling up to full-active-area fuel cells, to be made available for DOE testing.

Question 1: Approach to performing the work

This project was rated **3.2** for its approach.

- The General Motors (GM)-led team has an excellent approach to membrane electrode assembly (MEA) development and is addressing the technical barriers of cost, durability, and performance. The project is key to MEA development and meeting DOE fuel cell performance objectives. The GM-led project integrates efforts from Technische Universität Berlin (TU Berlin), Johnson-Matthey Fuel Cells Inc. (JMFC), the Massachusetts Institute of Technology (MIT), Northeastern University (NEU), and George Washington University (GWU).
- This project is nearly complete. It appears that significant science and technology accomplishments were made by all partners.
- The approach of this project is based on the well-established expertise of each participant in order to enable the dealloying protocol in practical nanoscale materials.
- The dealloyed catalysts appear to provide the desired manufacturability and long-term durability.
- The linchpin of this project is the core-shell alloy study by TU Berlin, from which a number of important publications were produced. The net outcome, however, led to a significant transition metal reduction in alloy through acid leaching, causing concern about the merit of such an approach. The Pt will undergo constant phase and oxidation state changes under polymer electrolyte membrane fuel cell operating conditions, and the transition metal will continue to be leached out. The team should verify at what level, if at all, the transition metal could be stabilized in such a structure.
- This is elegant research in electrocatalysis; however, it is on the type of catalysts that have been thoroughly investigated over at least a decade. There is still no definite answer to the question of whether dealloyed catalysts provide a long-term advantage over single-component Pt catalysts. It is unclear whether similar or better performance could be achieved using Pt catalysts with porosity induced by other means than leaching a transition metal.
- DOE funds a number of projects pursuing dealloying approaches. The claims of dealloyed core-shell structures that will be stable over long-term fuel cell operation are doubtful.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- The project team has made good progress toward exceeding the DOE fuel cell goals for MEA catalyst loading and durability. The $PtNi_3$ catalysts are well understood, and the GM team has done an excellent job in transitioning the advanced catalyst to MEAs.
- This project is making excellent progress in using expertise from multiple partners to derive fundamental understanding that could lead to improved catalysts.
- The team has been actively engaged in the synthesis and testing of the dealloyed catalysts. The researchers appear to be devoting a significant amount of time and effort toward the characterization and fuel cell testing of the materials. The distribution of particle sizes and shapes is huge. The data from transmission electron microscopy (TEM) cross-sectioning is quite weak. The samples are very heterogeneous and it is hard to draw conclusions. The surface areas of the catalyst were modest. The x-ray absorption spectroscopy (XAS) Pt shell penetration potential data is unproven. Strain measurements via extended x-ray absorption fine structure (EXAFS) are inaccurate compared to measurements made by diffraction techniques. The diffraction data presented was not analyzed for average lattice parameter or particle size. This data could be cross correlated to validate the x-ray absorption fine structure (XAFS) results. The accelerated stress test (AST) testing conditions were changed from 0.6 to 0.925 V to improve the durability. This is not standard protocol.
- The accomplishment was excellent and the team met most of the milestones. The performance improvement was clearly demonstrated. The characterization study relied heavily on an imaging method that is not a statistically meaningful. X-ray diffraction (XRD) and EXAFS studies are good, but they do not directly address the core-shell structure. The work by JMFC was somewhat hodgepodge and not different than what has been done by others in the past.
- The amount of experimental data over the past year has been impressive. At the same time, questions remain about the stability of PtNi (and PtCo) catalysts and, thus, their long-term advantage over transition-metal-free formulations. The impact of multivalent cations on ionomer conductivity is also unclear. Lowering the voltage limit to 0.925 V to ensure better durability, especially at lower loadings, does not seem like a viable approach.
- The accomplishments appear to be adequate in comparison to targets. It is not possible to say anything about durability. It also is difficult to know what the absolute status is. Manufacturing partner success is a plus.
- The progress of the project has been made by introducing additional Pt transition metal alloys besides PtNi. Particular improvements have been made by achieving better control of particle size distribution compared to the previous year.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- GM has led the project team well. The milestone/go/no-go chart gives a good overview of each institution’s role. The coordination with JMFC has worked well.
- The collaboration was excellent, with meaningful contributions from multiple institutions.
- There were a large number of participants, and it appears that all of them made progress.
- The project brings together many partners, with the goal of using expertise in different techniques. However, some of the results seem contradictory. The Pt/Ni core-shell structure is different for the catalysts prepared at TU Berlin versus GM. There appear to be inconsistencies between the EXAFS and TEM-energy dispersive spectroscopy (EDS) data. While the Ni content leads to increased initial activity, there is an optimal ratio, as implied by the volcano plot. The researchers need to characterize the end of life (EOL) catalyst to make their conclusions because these structures likely evolve considerably during use.
- While the level of contributions to the project by some partners, such as NEU and GWU, remains unclear, the project appears well integrated. This is a team of organizations with established leadership roles in their respective fields of research.

- The collaboration effort is satisfactory, although the coordination does look a bit compartmentalized. It is hard to tell how much cooperation and interfacing is occurring within this project.
- For some participants, particularly MIT, the role in the project was not obvious from the current report.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- The project is highly relevant to the Fuel Cell Technologies Office's (FCTO's) goal for fuel cell cost reduction and durability improvement.
- This project is very well aligned with the DOE objectives described in the FCTO Multi-Year Research, Development, and Demonstration Plan.
- The research being led by GM is critical for meeting DOE Hydrogen and Fuel Cells Program (the Program) goals. Addressing the operation of advanced catalysts in fuel cell stacks is particularly important.
- This project provides demonstrated performance on industrially relevant catalysts that can be manufactured on a large scale.
- The project mainly helped to validate already known mechanisms of dealloying and activity enhancement in a more controlled manner. It also implemented developed materials in MEAs. Protocols in Pt alloy catalyst pretreatment are now well established for practical use in fuel cell technology. The project managed to span from atomistic insight to integration of materials into fuel cell electrodes and stacks.
- This effort does appear to duplicate the Argonne National Laboratory (ANL)-led effort on dealloyed catalysts without achieving the same control of materials synthesis or level of characterization. However, it does offer more fuel cell testing.
- This project is in alignment with the goals of the Program.

Question 5: Proposed future work

This project was rated **2.9** for its proposed future work.

- Proposed activities are in agreement with the duration of the project, which ends in September 2014.
- A thorough assessment of the effect of transition metal(s) on the electrode ionomer and polymer electrolyte membrane should have been one of the primary objectives of this project from its inception. That effect should be studied between now and the project end date in September. If that is not planned, inclusion of that task in the ANL-led MEA project is the second-best option.
- The investigation of core-shell alloy stability should really have been completed within the framework of this project. In fact, it should have been done at the rotating disk electrode (RDE) level in the beginning of the project because it serves as the foundation for the rest of the effort.
- The proposed future work transitions to an ANL-led project. MEA/stack development is expected to continue with a focus on the PtNi system. This transition is not entirely clear.
- The team is aware of some of the shortfalls of the effort and has defined a future work effort to attempt to overcome them.
- A better understanding of the working catalyst is needed.
- The stability testing should be completed.

Project strengths:

- There is a strong team that includes leading institutions from industry and academia. The project has shown the ability to employ fundamental principles in material development.
- A strength of this project is its combined synthesis and fuel cell testing rather than reliance only on RDE data.
- The combination of catalyst synthesis, testing, and characterization techniques is a strength of this project.
- Strengths of this project include its milestone delivery and multi-institution collaboration.
- The main strength of this project is the high quality and thoroughness of the performed research.

- GM and JMFC have formed a strong group.

Project weaknesses:

- The lack of control throughout the project of the particle size distribution and the homogeneity of elemental composition turned out to be a critical factor that limited the ability to interpret results.
- The main weakness is the reliance on the still-unproven long-term benefit of dealloyed catalysts, especially in the ionomer environment of the fuel cell cathode.
- Most characterization presented is on the initial catalyst, not the working catalyst.
- There is a lack of control over materials homogeneity.
- No clear strategy was identified for long-term core-shell catalyst stability.
- The transition to ANL is not clear.

Recommendations for additions/deletions to project scope:

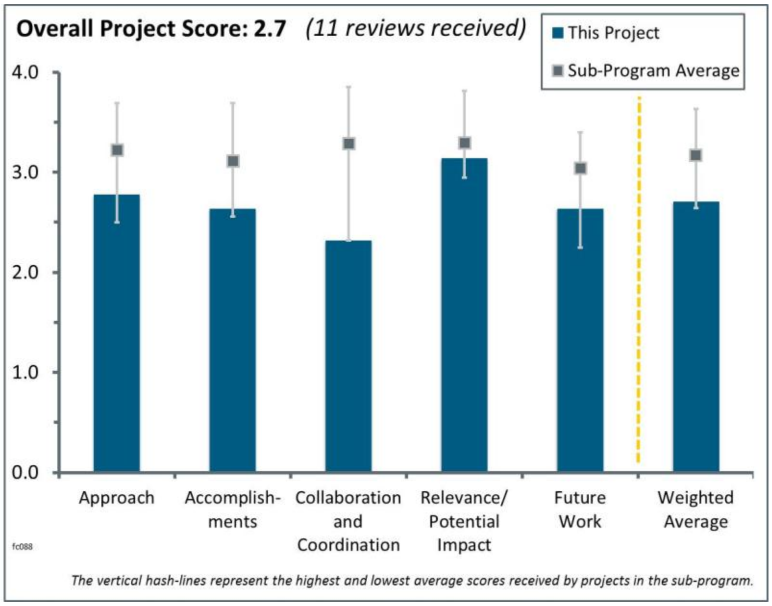
- The researchers should relate the EXAFS, XRD, and TEM-EDS data to derive a better picture of the working catalyst.
- The project team should wrap up the project with some definitive conclusion, particularly on the prospect of long-term stability.
- The project is ending soon, and the remaining proposed work is appropriate in scope for that short period of time.
- The team should continue the MEA development work with ANL and focus on stack testing at GM.

Project # FC-088: Development of Ultra-Low Doped-Pt Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells

Branko Popov; University of South Carolina

Brief Summary of Project:

The goal of this project is to develop a low-cost catalyst with optimized average mass activity, stability of mass activity, initial high current performance under hydrogen/air (power density), and catalyst and support stability able to meet 2017 U.S. Department of Energy (DOE) targets. The objectives are to: (1) develop a cost-effective, high-volume synthesis procedure to manufacture highly stable activated carbon composite catalyst (A-CCC) support, and (2) to develop low-cost procedures to synthesize a catalyst with enhanced activity due to the synergistic effect of pyridinic nitrogen catalytic sites from the support and suppressed Pt-lattice catalyst.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **2.8** for its approach.

- The approach is focused on overcoming barriers by lowering the cost of Pt and developing a more durable catalyst support combination.
- The approach is to develop the non-corrosive fuel cell support to enable high mass activity with low platinum group metal (PGM) loading that is close to the DOE target.
- The hybrid catalyst approach to use a stabilized support with Pt deposited on top looks like a promising approach to improve the stability of the Pt nanoparticles. This approach combines the stability of the support and the anchoring site to improve the stability of catalysts in the fuel cell environment.
- The principal investigator (PI) should consider whether the approaches tried over the past two years are likely to achieve targets in a realistic fashion. If not, then the PI should make a well-reasoned move to another approach. It is known that shrinkage is still a problem; activity loss during tests is also still a problem. The approaches in this work have been to pyrolyze materials with carbons to place metals in the carbon, to vary temperatures of pyrolysis, to modify the surface of the carbon to include oxygen or nitrogen containing groups, or to use a polyol and modified polyol process (but no details were presented on this). This is not a winning approach, especially not when attempting catalyst and support development and potential scale-up.
- The approach is based on creating a transition-nitrogen-carbon electrocatalyst and using it as support to deposit Pt and to create a Pt alloy catalyst. It is unclear why so many synthesis steps are needed to achieve another type of PtNi material like that studied by other projects. In addition, even though the initially created materials meet DOE target goals, no clear progress has been made relative to last year’s report. The best material so far is the same as reported last year. The uniqueness of the approach is described by vague terms such as “controlled heating,” “modified” synthesis, etc.
- The approach of this project as stated appears to combine two synergistic effects to address improved catalyst support durability and improved catalyst activity. It was not entirely clear from the presented material what the experimental evidence is for whether such synergism really exists. The Pt-A-CCC still has carbon corrosion to contend with at the highest potentials (1.5 V) expected during start-stopping of vehicles. It is therefore not clear how this approach will provide any significant advantage from a durability standpoint. It is good that the project has a focus on both the catalyst and the support. This is an interesting

concept. The Pt-free activity of the support is quite surprising. However, it is not clear how, in the end, one gets a catalyst that is intrinsically different from commercial PtCo/graphitized carbon, except for the presence of Co doping of the support. One advantage of the approach stated on slide 8 is that it increases the Brunauer-Emmett-Teller (BET) surface area and pore size uniformity for uniform Pt deposition. The BET surface area reported is only moderate at 200 m^2/g of support material, and the Pt catalyst surface area reported of 31 m^2/g-Pt appears a bit lower than commercial Pt/C on highly graphitized carbon supports.

- This work focuses on a parallel improvement of catalyst supports and Pt catalysts. On the support side, the researchers used doped material with pyridinic nitrogen sites to improve the Pt dispersion and treating the support under high temperature to increase stability. On the catalyst side, the researchers sought the synergic effect of Pt/non-PGM materials for oxygen reduction reaction (ORR) catalysis and attempted to maintain high Pt dispersion via Pt-transition-metal interaction. The development concept is mostly sound and reasonable although it is not necessarily innovative, because most of the ideas have been known in the field for quite some time. The PI should address the following concern regarding his approaches: the synergic effect between Pt and non-PGM materials needs to be elaborated through the experiment, and the contributions -of each of the components at different regions (kinetic and mass-transport limited) are unclear. The PI should also present experimental data to elucidate this point, particularly on the “support” side.
- The team is well focused toward addressing the key barriers of performance, cost, and durability. The work to develop alloys appears novel and logical, based on the carbon composite catalyst (CCC) fabrication approach, and it has been reasonably successful. It is of moderate concern that most or all of the polarization curves used to show the effects of durability accelerated stress tests (ASTs) are presented iR-free, suggestive of possible high-frequency resistance (HFR) increases. To eliminate this concern, the PI should present results with measured, rather than iR-free, cell voltages. Additionally, it is concerning that in some cases, hydrogen/O_2 polarization curves are shown rather than hydrogen/air; hydrogen/O_2 curves can mask degradation due to changes in electrode porosity and/or hydrophilicity, which can occur after ASTs. It is recommended that hydrogen/O_2 measurements be limited to evaluation of ORR activity and performance evaluated only under hydrogen/air.
- The approach of combining activated C with doped Pt is good for trying to lower Pt loadings, but close inspection of the approach generates some consideration of whether there are too many processes involved and what time is involved for each process. The reviewer wonders what the cost would be of both pyrolysis followed later by Pt doping. There appears to be a long heating time required for obtaining the single phase of PtCo for the doping (2–4.5 hours). Furthermore, the best activity catalyst in this project involves leaching for 12 hours. The project could benefit significantly from having a major industrial catalyst supplier as a partner to identify which processes are tenable from a manufacturing standpoint, and what lengths of time are realistic for each step. The reviewer questions whether the materials can be practically made at high volume.
- The project is focused on the development of Pt/Co catalysts through the embedding of Co in the C particle, but there are also aspects of catalyst development that seem focused on either non-precious catalyst development or the use of active support materials for improved Pt ORR. The order and arrangement of the slides as well as the lack of clarity in the presentation and apparent disregard for the required guidelines make this and every other aspect of the project hard to judge appropriately. The presenter claimed a benefit by putting the Pt down in a subsequent step and then getting Co into Pt through annealing, but from a fundamental scientific standpoint (and from the data presented), there is no reason to believe a significant improvement would be obtained compared to standard Pt/Co catalysts.
- The PI is adhering to the project’s statement of project objectives (SOPO) but is resistant to evaluating materials on updated durability protocols. The hybrid catalyst is showing good results.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.6** for its accomplishments and progress.

- Excellent progress has been made toward generating high-performance alloy-CCC electrocatalysts. Leaching development has yielded substantial improvements on kinetics and membrane electrode assembly (MEA) performance. It is unclear, however, why the leaching results in substantial improvements in

activity, and this should be studied further for possible further improvements in activity. The development work to generate homogenous Pt distribution via support surface modification appears to have been successful.
- Very good progress has been made toward synthesis of doped supports and combined catalyst-support structures. Durability and surface area of support was significantly improved versus commercial Pt/C. Synthesis of uniformly dispersed small Pt nanoparticles is not really an accomplishment—it has been done many times using other synthesis methods.
- The project has shown a catalyst (30% wt.%) with reasonable mass activity in a fuel cell MEA. While many catalyst projects do claim high mass activity in rotating disk electrode (RDE) tests, those claims are hard to realize in an MEA—this project has achieved that.
- Slide 21 shows that most technical targets have been met with a doped Pt/A-CCC cathode catalyst.
- The accomplishments of this project are generally considered good, based on the performance data provided. The PI should address the following questions regarding the achievements:
    - Catalytic activity of the “support” measured by RDE was reported. The PI should have also included the “support” activity study measured in MEA at the single-cell level.
    - The PI demonstrated an excellent improvement in stability against commercial Pt/C material. Representative data of the commercial Pt/C catalyst/MEA should also be included in the presentation for comparison.
    - The catalyst study demonstrated good Pt/Co alloy formation in situ. However, a better scientific rationale should be included to support such an observation.
    - The catalyst demonstrated good stability under a relatively mild cycling condition (0.6–1 V). For the Pt-based catalyst, a more severe aging condition should have been used.
- The 40% doped Pt/A-CCC catalyst was able to meet targets for the 1.2 V hold test. This is an improvement over the Pt-only results last year when the mass activity loss was 47%. Furthermore, the hydrogen/air iR-corrected performance at only 0.1 mg/cm^2 Pt appeared good (it would be helpful to see a Pt/C baseline). The team achieved 0.17 A/mg Pt for Pt/A-CCC after 400 hours at 1.2 V, and 0.23 A/mg Pt for Co-doped Pt/A-CCC after 30,000 0.6–1.0 V cycles. The end-of-test target is 60% of 0.44 A/mg Pt or 0.264 A/mg Pt. Therefore, the doped catalyst is just below the end-of-test targets after these cycles. However, there was improvement in mass activity versus last year (0.38 A/mg at the beginning of the test and 0.20 A/mg at the end of the test for 0.6–1.0 V cycling). The doped catalyst had 79 mV of loss at 0.8 A/cm^2 after 30,000 0.6–1.0 V cycles—this is beyond the targeted 30 mV loss. One point of confusion exists: the doped catalyst is described as having 0.408 A/mg Pt on slide 16, and then a doped catalyst is said to have 0.35 A/mg Pt on slide 19. This discrepancy should be sorted out. Catalysts are progressing toward end-of-test targets through incremental improvements in doping and leaching.
- The presenter could not explain the whole presentation in the time allotted, so the following comments are based on presentation material only. Catalyst durability—as indicated in the previous 2013 comment, the support should be evaluated based on new DOE protocols instead of a 1.2 V hold. Milestone—according to the 2013 presentation, the down-selected catalyst scale-up and short-stack testing were scheduled in Phase II. These two milestones could be valued points to evaluate the practicability and manufacturability of any type of new catalysts.
- It appears that a substantial amount of work has been accomplished with good progress toward meeting the project’s assigned targets on performance and durability. It is confusing, however, that the polarization curves shown to declare progress toward the inverse specific power density target of 0.44 A/mg (PGM) all show an iR-corrected voltage scale. The inverse specific power density should be determined from as-measured polarization curves, not iR-corrected curves. The MEA anode and cathode loadings are not always stated, either.
- The activities of the best catalyst show insignificant improvements over commercial Pt/C, with a few metrics meeting the DOE 2017 target. No comparison is shown to the state-of-the-art Pt/C or the best Pt alloy catalyst. Even though the project reports on multiple characterization venues, no durability studies of aged materials are reported. The progress since 2012 and 2013 is very limited.
- From the presentation and the PI’s remarks, it is unclear whether any meaningful advances have come in the past year. Much of the issue comes from the presentation itself, where the PI took 10 minutes to go through the first five slides and had less than half of his allotted time to discuss any data or findings from the project. He was unable to get through the last 10 slides of his presentation. From the table on slide 21, it

seems that the researchers have been able to approach the performance of state-of-the-art PtCo/C catalysts but are still far behind other advanced alloy nanoparticle approaches.
- This was very unclear from the presentation. Too much 2013 data was shown. The presenter indicated changes in the targets, but not why they were made or the impact on approach. The PI spent too much time railing against earlier presenter comments.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.3** for its collaboration and coordination.

- There is good collaboration between universities involved in this work. If funding allows, it would be helpful to have an industrial partner as a collaborator to evaluate catalysts' performance in fuel cells.
- The list of collaborators is very strong and has promise, but the majority of the results reported come from the lead institution, with very little information available from all the subcontractors. It is not clear what company/institution out of the team is leading a scale-up effort, if any.
- There is mostly strong collaboration with academia, but not with an automotive original equipment manufacturer (OEM) (Hyundai Motors). OEM testing of these catalysts is recommended.
- University collaboration is strong. The program needs collaboration with catalyst makers and stack integrators.
- The project has a reasonable set of collaborators. However, it is unclear what the key contribution is for each collaborator. Dr. Popov's group seems to be doing (as shown in the presentation) the majority of the work, while other collaborators are providing some support in analysis. The synergistic interaction of these various collaborators so this project can achieve the targets is unclear.
- The collaboration and coordination appeared to be acceptable. A slide with collaborations was shown. Whether these are partners or not was unclear. The technical aspects they contributed to were indicated, but not during the presentation. It seemed more like single investigator work, which perhaps it predominantly is.
- The level and type of collaborators are reasonable. It would be useful to have some collaboration with an established MEA integrator (industry or national laboratory) to validate performance at a second site.
- The collaborations throughout this project are little noted in the slides. It appears that the project had characterization done by three parties outside the University of South Carolina (USC): University of Illinois, Chicago; University of Illinois, Urbana-Champaign; and Clemson. These collaborators did ICP, TEM, HRTEM, and XEDS. Some other organizations designed test cells to USC specifications. Essentially all "collaboration" was realized through tasks appointed by USC. No automotive OEM or stack OEM collaboration existed. Other catalyst projects have included a partner for scaling up manufacturing quantities (e.g., Johnson-Matthey Fuel Cells Inc. [JMFC] in the General Motors catalyst project). That does not exist in this project.
- It is unclear if any of the presented work was performed outside of South Carolina or what the listed subcontractors specifically contributed to the project. The project would benefit from the inclusion of a catalyst company and an OEM, and it might benefit from other groups with enhanced characterization or MEA fabrication/testing capabilities.
- Most of the work appears to be centered at USC, with no national laboratory or industrial partners. What other work is done is restricted to materials characterization.
- The collaboration in this project is weak. The PI's collaborators are limited to microscopic imaging or analysis. The vendors should not be listed as collaborators. The PI should include other institutions, particularly industrial OEMs, in catalyst and MEA evaluations.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.1** for its relevance/potential impact.

- The project is relevant to DOE goals on improving catalyst activity, durability, and stability.
- Durable and high-performance catalyst/support systems are needed with low-PGM loading.

- This project is well aligned with DOE targets on cost, activity, and durability.
- The project is well aligned with the DOE Fuel Cell Technologies Office's goal.
- The project, with the data presented, shows promise in improving the stability of the Pt catalyst. The key is understanding how to improve the high air performance and document improvement against the state-of-the-art Pt/C catalysts.
- The project is focused on low-loaded Pt catalysts with required durability. This is perhaps the top need of the community at this time. The project lacks a defining advantage over other approaches being pursued.
- The approach and progress aside, this project is working on the most relevant topic to DOE's fuel cell effort, which is the development of a durable, high-activity oxygen reduction catalyst. If such a thing exists, the entire stack could be decreased in size, reducing cost for Pt, membranes, gas diffusion media, and plates. The cost of the air handling system may also be decreased if catalyst activity could be leveraged for lower pressure. The project has combined concepts for non-PGM materials that are active for oxygen reduction, and Pt modified with base metals for higher activity. Both streams have been identified as relevant in other projects. The only difference in this project is that the investigators have combined the two concepts.
- If successful, this project would provide an alternative approach to generating Pt-alloy catalysts dispersed on graphitized carbon-type supports with some potential additional support benefits. However, it would still have the disadvantages of carbon corrosion at the high potentials expected in start-stopping; the costs associated with the high-temperature processing steps of dispersed catalysts; and loadings not much different from other methods being pursued that do not have these limitations, such as the 3M electrode approach. The long time (12 hours) of leaching and annealing for the best catalyst preparation will significantly add to the manufacturing costs of this catalyst on any reasonable scale. One question is whether a faster process can be found with the same effectiveness.
- The project is certainly progressing in the direction of DOE and DOE Hydrogen and Fuel Cells Program goals, but it is not going to contribute strongly.
- The project is relevant to DOE's objectives in creating a durable, active, low-Pt-content catalyst. As a result of very insignificant progress, no significant impact is expected, considering this is the last year of funding.

Question 5: Proposed future work

This project was rated **2.6** for its proposed future work.

- The future work is logical and rational and has quantitative performance and durability goals. Durability with updated protocols should be checked.
- Overall, the future work advances each of the tasks. However, a question arises from the timeline slide: it is unclear whether there is any mechanism or time allotted for "circling back" from any newly understood result to insert a new approach or modify the plan of any given task. The tasks seem to be laid out very linearly. The target catalyst performance characteristic (ii) listed for Task 4 (slide 22), according to the revised SOPO dated 1/23/2014, says "initial high current density performance of at least 1.5 A/cm^2 at 0.6 V iR-free." This should be a goal stated in terms of as-measured cell voltage, not iR-free, because the electrode impedance and how it changes with current density and operating conditions need to be understood. This is a critical property of any new catalyst. The durability testing should also include voltage cycling to 1.5 V, not just 1 V, because this will evaluate the most likely serious flaw of this approach—carbon corrosion at very high potentials generated by stop/start effects. This should be done sooner rather than later, because it will likely be the most serious problem to be addressed.
- There is little time remaining in the project, but for the most part, the tasks identified are ones that are needed. The doped catalyst may only be a few optimization steps from meeting both end-of-test mass activity and 0.8 A/cm^2 performance targets. The one thing that needs to change involves "optimization of high volume production procedures." The partners, as listed, do not have the experience to complete this task, because nobody listed is a high-volume catalyst producer. It would be good if someone at DOE could manage to help the investigators work with a partner like JMFC/TKK/Umicore/BASF, or some party with that expertise. A cost analysis of the final process would also be helpful.
- The proposed future work sounds good. It would be good if the project can clearly document whether there is any change in specific activity (microA/cm^2 Pt) and any loss of Co from the catalyst during the durability cycling.

- The proposed work is adequate, considering the duration of the project. Because no obvious progress has been made with the current best material, efforts should be put into durability and scalability studies.
- The future work appears appropriate, based on the stage of the project.
- The future work is focused on overcoming barriers identified during the previous year. Identifying the reasons for enhanced mass activity of the Co-leached Pt catalyst should be a focus of the future work.
- It will be beneficial to have the industry-led evaluation of the technology in addition to the DOE deliverables.
- Future tasks such as the scale up of synthesis and MEA fabrication and testing to meet the 0.3 A/mg Pt target are not in line with the DOE out-year targets that speculative materials should be targeting. It is unclear how to best refocus effort in this project, but the key issue should be to focus on higher catalyst performance and improved activity before worrying about either scale-up or fuel cell testing.
- There was no time remaining for discussion of future work and rationale. The speaker went way beyond the time limits.
- The proposed future work is weak. At this stage of the project development, the PI should be able to elaborate on one or two topics to focus the effort based on the lessons learned. Describing the future work by reiterating the initial proposed tasks without including new scientific insight renders it generic.

Project strengths:

- The project features a good concept in combining two different oxygen reduction activity ideas into one: non-PGM activated carbon composite and base-metal-doped Pt. The project team understands well how to manipulate on a small scale the process parameters needed to increase the mass activity of the materials, both for beginning-of-test and end-of-test. There has been year-after-year improvement. The project ably used surface modification of C to improve dispersion of Pt, which is not an easy thing to do.
- If experimentally demonstrable, the synergy of the ORR active support combined with the Pt core-shell catalysts deposited on it is a real strength.
- The project has a strong team, as well as strong synthetic and characterization capabilities.
- This project proposes a new, very interesting approach for doping Pt with a transition metal.
- This project closely meets the DOE targets on activity and support durability.
- The project features a good approach and a strong team.
- Strengths of this project include the reported performance and the strong relevance to DOE’s goal.
- The project focuses on the key barriers of performance, durability, and cost.

Project weaknesses:

- It is unclear whether the approach offers anything above or beyond state-of-the-art PtCo/C catalysts. A major concern for the project is the PI’s lack of concern for guidelines and his inability to present his work in an adequately reviewable format. The presentation packet has 59 slides, while the guidelines stated a maximum of 28. The inclusion of such significant but unorganized data in the supplemental slides constitutes either an inability to determine the relative importance of the work presented or a disregard for reviewers’ time and effort. The PI was unable to present the majority of the most important slides regarding results during the allotted presentation time and spent undue time either preaching or going through background information of low value. The slides themselves left much to be interpreted, and despite spending more than twice as much time on this review than on any other, this reviewer still has twice as many unanswered questions. The PI’s behavior with the session moderator also was inappropriate.
- Weaknesses include the lack of automotive OEM collaboration and the lack of catalyst supplier collaboration for scale-up. All collaboration was directed by the USC. Numerous processes appear to be involved in making the catalyst, including pyrolysis for the A-CCC, chemical leaching to remove metals from the A-CCC, and the doping of Pt, presumably followed by some form of leaching to remove excess metals. No economic analysis has been presented to show whether all these processes add significant cost that would offset the lowering of precious metal loading.
- The presenter and the presentation material are the biggest weakness for the project. It was hard to follow the speaker. To further complicate the matter, the catalyst types and activities were not clearly mentioned. A simple table of all catalysts prepared and tested with electrochemical surface area, mass activity, specific

activity particle size, and other key parameters would help. It is almost impossible to get these data without digging through various parts and pieces of the slides.
- The project pursues very difficult and convoluted synthetic routes with an unclear purpose. No comparison is presented with the state-of-the-art Pt-alloy material. The Pt-C interaction and the stability of carbon support have not been carefully studied. Very incremental progress has been made in the last two years.
- Cobalt leaching, both from the support and the core of the core-shell nanoparticles, may compromise fuel cell durability. It is another approach to modify the catalytic activity of Pt by introducing a transition metal.
- There is weak collaboration with OEMs and catalyst suppliers.
- The targets are not rigorous enough to reveal the real potential issues with this catalyst/support approach. They should involve more severe testing to determine sooner the extent of the materials issues.
- The project has much more data than its interpretation. The project is also lacking the industry evaluation/verification.
- Weaknesses of the project include the scientific rationale and limited collaboration.

Recommendations for additions/deletions to project scope:

- The researchers should add voltage cycling durability tests to 1.5 V for the durability as soon as possible. They should also add tasks to evaluate the MEA performance as a function of PGM loading, covering the range of 0.125 (total from anode and cathode) to 0.35, to demonstrate the impact of electrode thickness effects, water management, and impedances on high current density. The researchers should be sure to show the as-measured polarization curves, not just the iR-free voltages.
- Mass-activity evaluations need to be complemented by specific activities and Pt surface-area calculations. Otherwise, it is unclear why Co leaching from the Co-modified catalyst leads to improvement in mass activity. It is unclear if it is just surface area effect. Durability tests need to be complemented by testing the fuel cell in “start-stop” conditions (i.e., between 1 and 1.5 V).
- The project could benefit from an assessment of actual current status and a management review of the proposed plans to achieve targets. This should be a go/no-go meeting, and some technical catalyst experts (especially with regard to commercialization) should make the assessment.
- The project is always reporting hydrogen-air performance as iR-free voltage; it is unclear why the researchers cannot report the as-measured cell voltage. The reviewer wants to know if they can work with the newer material set for membranes and gas diffusion layers to improve performance rather than trying to correct for it.
- One important addition needs to be made: an industrial catalyst partner needs to be added to scale up the catalyst manufacturing and to provide perspective on whether the processes being prescribed are suitable for high-volume manufacturing. Stack or automotive OEM collaboration would be helpful and should be added in the last stage of this project.
- The project team should focus on one or two promising systems and demonstrate stability at more demanding conditions.
- The team has to focus on the durability and scalability of the best material to-date.
- The team should broaden collaborations.
- This project should be discontinued. Outside of this, any further effort should be focused just on catalyst development and characterization without scale-up or large-scale fuel cell testing. In the future, the material presented has to be presented in a cleaner, more cohesive manner.

Project # FC-091: Advanced Materials and Concepts for Portable Power Fuel Cells

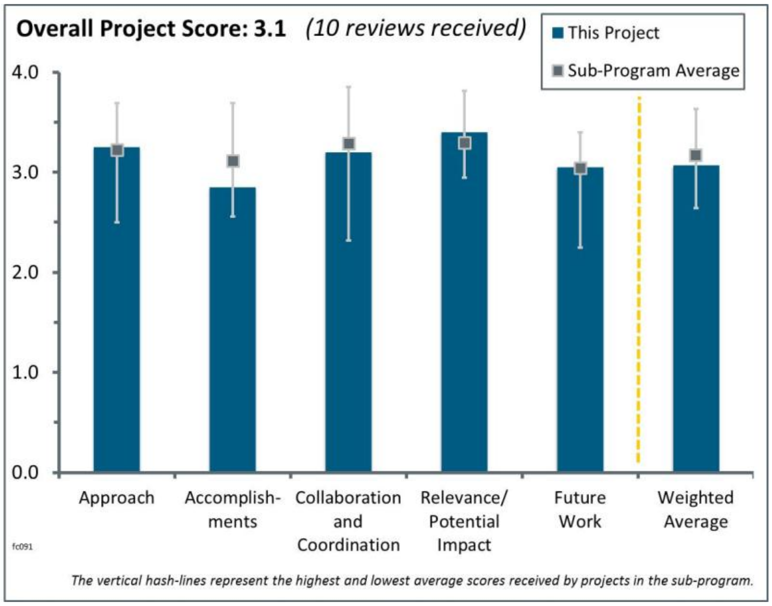
Piotr Zelenay; Los Alamos National Laboratory

Brief Summary of Project:

The objective of this project is to develop advanced materials (catalysts, membranes, electrode structures, membrane electrode assemblies [MEAs]) and fuel cell operating concepts capable of fulfilling cost, performance, and durability requirements established by the U.S. Department of Energy (DOE) for portable fuel cell systems. The project will ensure a path to large-scale fabrication of successful materials.

Question 1: Approach to performing the work

This project was rated **3.3** for its approach.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

- This project involves a variety of activities related to fuel cells using alcohols or other C-containing molecules as fuels for portable power systems. Specific focus areas include improved PtRu anode catalysts and hydrocarbon membranes for direct methanol fuel cells (DMFCs) as well as improved catalysts for direct ethanol fuel cells (DEFCs) and dimethyl ether fuel cells (DMEFCs). The project also includes materials characterization and MEA performance testing. The project is near the end of its term. The project is well designed, focusing on technical milestones relating to barriers from the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan (MYRDDP). The specific work tasks are a bit diffuse; for example, alternative fuel research is to a large degree separate from DMFC research, but all of the work helps support the DOE goal of improved portable power generation.
- The combination of catalyst, membrane, and electrode development and the investigation of three fuels toward the targets is strong.
- The project was well designed. DOE made good choice. The barriers are clear.
- The overall approach is sound. All critical aspects of catalysis, membrane, and MEA for alternative fuel fuel cells are included. One thing that could be improved is to clarify the purpose and interactions of the multiple directions/institutions on catalyst development. For example, in methanol oxidation catalysts, Johnson-Matthey Fuel Cells Inc. (JMFC), Los Alamos National Laboratory (LANL), Brookhaven National Laboratory (BNL), and the University of Delaware (UDel) all have seemingly isolated projects. The interconnection of each direction is not clear. BNL and UDel catalysts have remained on the model catalyst scale and have never been benchmarked against the newly developed JMFC or LANL catalysts, so it is very difficult to judge the merits of the UDel and BNL catalysts.
- The project has a wide scope, including DMFC anode research, electrode structure development, hydrocarbon membrane development, and alternative fuels for portable fuel cells. This wide scope may prevent the project from making significant progress. Reduction in catalyst loading and cost would be an important area of focus for the portable power field. Expensive catalysts and high loading are still used for DMFCs and DME fuel cells. PtRu nanotubes and PtRu nanowires are good pathways to reduce the catalyst loading, but improvement in durability is not known. Last year, the project showed high DMFC performance with ultra-thrifted anode PtRuSn/C with only 0.3 mgPt/cm^2 loading using 2 M MeOH. It is unclear why a different anode catalyst (advanced anode catalyst [AAC] 1:4 PtRu/C) was the focus of this year’s DMFC work and used for stack testing by SFC instead. It seems that the lower-loading PtRuSn/C would have been a better choice. LANL should strive for a low-loading catalyst that is durable and performs well at higher methanol concentration. These criteria are important to aid in the

commercialization of fuel cells. The advantage of fuel cells is the longer operating time; therefore, the DMFC system must be developed for operations at higher MeOH concentration to increase the energy density of DMFCs. An impressive set of characterization tools is available and has been implemented in the project.

- The approach to adapt improvements in catalysts for hydrogen fuel cells using nanostructured catalysts for DMFCs and DEFCs focuses on a key barrier to commercialization: cost. The bifunctional catalyst approach is logical; the use of oxides such as CeO_2 to enhance oxidation is a good approach. Block copolymer work is a good approach to try to reduce methanol crossover and improve performance. The work on alternative fuels (i.e., ethanol and DME) is appropriate. The researchers need to look at fuel utilization, anode recycle schemes, and exhaust/emissions for DMEFCs.
- The multidirectional approaches taken by the team for the completion of all tasks are adequate. All the technical barriers have been addressed appropriately. The responsibilities for anode, membrane, alternative fuel development, and performance/durability tests were given to the research teams with significant experience and strength in the respective areas of research.
- LANL is targeting the main challenges of DMFCs: reducing the high amounts of expensive catalysts currently needed, reducing methanol permeation, increasing overall efficiency, and increasing durability. These aims are achieved mainly by developing new anode catalysts and new membranes. For direct DME fuel cells and direct ethanol fuel cells, improved catalysts are developed to improve performance.
- There appears to be a lot of work being reproduced—Pt:Ru ratio optimization has been carried out numerous times. One of the most interesting things with EtOH fuel cells should be the extent of conversion to CO_2, but not much emphasis or work has been done here. It was good to see some long-term testing, but of most interest would be a post-mortem analysis of these materials (—determining where the decrease in performance came from, how much catalyst was lost, or how much the mass transport resistance increased). Justification for the different membrane chemistries is not given; it is unclear how block chain length affects the conductivity/permeability ratio. LANL was criticized last year for a lack of long-term testing; the rationalization that it will tie up precious resources is unsatisfactory for a $10 million four-year project Choosing only one system to test provides little insight to the community. The durability of these systems is one of the biggest open questions, and it is given minimal importance.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- LANL is making consistent progress toward DOE goals. The DMFC anode work with JMFC is providing optimized formulations with high activity at low precious metal loadings. The performance target is very nearly met. The nanotube/nanowire catalyst microscopy was very well done, and the catalysts appear to have high activity. All the approaches discussed for improving catalysts appeared to provide incremental improvements. The hydrocarbon membrane work also provided incremental but significant improvements, with favorable combinations of methanol blocking and ion transport demonstrated. The ethanol and DME oxidation work was interesting, but it needs a tighter focus on mass balance to account for all the various pathways that may be followed for fuel oxidation. If ethanol oxidation occurs with only 40% efficiency, it will be important to consider why ethanol might be desirable as a replacement for methanol.
- The team has achieved the stack milestone using the AAC. It will be good to see the use of a low-cost tetramethyl bisphenol A (TM) membrane in stack testing. With N115 in the stack, it is hard to understand whether the low-cost membrane will be able to function in the stack. The team should also determine the stability of these new anode catalysts under anode starvation, which is important to understand.
- Good progress has been made on the JMFC DMFC catalysts, LANL DME catalysts, and Virginia Tech hydrocarbon membrane thrusts. The BNL and UDel catalyst projects each tried some seemingly new combinations, but it is difficult to judge their impacts on the overall project based on the limited data presented. The potential poison effect by Cu in the UDel catalyst project was raised last year, but this issue was ignored by the team.
- The new PtRu nanowire catalysts look promising, but scale-up to 9 mg per batch is not a demonstration that multigram quantities could be produced if the technology were to be commercialized. A nice suite of new multiblock copolymers was prepared, some of which showed all three desirable properties of water uptake,

ionic conductivity, and lower crossover. Because it is known that breaking the C-C bond in ethanol is extremely challenging at low temperatures, the electrochemical data must be combined with product analysis for meaningful evaluations of these new catalysts. The progress with the DDMEFCs was outstanding.

- The researchers have achieved good advancement in DME activity over the past year and over the life of the project. Good improvement in DMFC performance is indicated for the TM membrane (slide 12). However, this membrane has high resistance, which raises questions because others have found membrane resistance is much more important than methanol crossover for determining performance. It is not clear whether cell voltage is iR-corrected in this figure. (If it is iR-corrected, then cell performance for the TM membrane would not be improved, due to the resistive losses from membrane). If it is not iR-corrected, the improvement from decreased crossover is larger than others have observed. It is not clear what has been done in the past year, but overall progress has been good. Improvement in DMFC performance does not appear to have been made over the last year; it is still 40 mV from the target. It is not clear what new work has been done with membranes since last year.
- Significant progress has been made in all fields of work. In particular, the high DMFC performance with low anode catalyst loading is very impressive, even if the milestone has not quite been reached yet. It would be desirable to have methanol permeation data for these measurements. A very high methanol utilization of 0.96 was assumed without any proof. The newly developed membranes look very promising, but measurements comparable to the measurements with the new anode catalysts and methanol permeation should be performed to show the effect of the membrane under fuel cell operation conditions. Progress in DEFC catalyst research is being made, but this is shown on a model system only. Fuel cell measurements should be done here as soon as possible. Progress on DDMEFC catalysts has been made and performance similar to a DMFC has been achieved. Measurements with DME ware made under significant pressure (anode 26 psig, cathode 20 psig); the effect of this on balance of plant (BOP) efficiency should be evaluated to assess if the BOP efficiency of 0.9 stated as an aim at the beginning can still be reached.
- Overall, the project team has made good progress in all areas, but not necessarily toward DOE goals. Durability testing in a stack by a DMFC developer is good. However, a 1 mg/cm^2 AAC (PtRu/C) was used for the testing instead of ultra-thrifted PtRuSn/C (0.3 mg/cm^2). It is not clear what the wt.% of metal was in AAC and what type of carbon was used in the support. It was also not clear how it was determined that the optimum Pt:Ru ratio was 1:4 for fast dehydrogenation and efficient CO removal. It has been reported in the literature that 1:1 PtRu was the optimum ratio. Also, a relatively low methanol concentration was used for testing; a higher methanol concentration needs to be used to increase the energy density of DMFCs and make them competitive to batteries. The work on PtRu nanotubes and PtRuCu nanowires is very interesting. It was unclear whether the synthesis method was galvanic displacement, how the ECSA for these catalysts was determined, whether there was any evidence of Cu leaching from the catalyst, and how this affects methanol oxidation over time. The scale-up of PtRuCu nanowires was notable. Catalyst development for ethanol oxidation is interesting, but the mechanism of ethanol oxidation on these oxide catalysts is unclear. Also unclear is the role of CeO_2 and why it enhances the activity of PtML/Pd/C. The hydrocarbon membrane appears to have good properties, but it does not seem that the membrane has much better methanol crossover than the industry standard. It would be nice to see data for higher methanol crossover and electro-osmotic drag. Furthermore, the fact that HFR increased with time during life testing does not indicate a stable, durable membrane. It is unclear whether this was a membrane issue or an interfacial resistance issue, and whether the ionomer was used in the durability testing of the membrane.
- Improvements in DMFC performance are incremental. Project goals are not very ambitious. LANL has done a nice job of showing the feasibility of DMEFCs, but there is little innovation here; the MEA that worked the best was essentially the same as the DMFC MEA. How to use DME with a high utilization seems like the most important question now, and investigators have given it little thought. A stoich of even 1.3 would be disastrous; it is unclear whether one would just vent this to the atmosphere or oxidize it in a reactor—that negates system simplifications. The essential membrane performance metric is the ratio of conductivity/permeability; then original equipment manufacturers (OEMs) can choose the thickness that optimizes for their application. This ratio is never given and the two parameters are always given separately, making it hard to evaluate their progress.
- It is unclear whether the 0.6 V at 150 mA/cm^2 MeOH-oxidation is reachable before the project ends in September. Temperature or loading does not seem to provide the necessary boost, and the increase in temperature would increase the performance boost at the cost of durability. There does not appear to be a temperature or pressure set point in this performance target—there should be. The mass activity target has

been achieved according to the principal investigator (PI), but it is not clear whether the mass activity is based only on the anode platinum group metal (PGM). The cathode loading was very high. LANL showed good stack and membrane results. The nanowire looks promising, but at 19 mg/batch, scale-up seems far away (despite claims of demonstrated scale-up from 5 to 19; this is not nearly manufacturing scale). The quantities necessary for commercialization are not clear.
- The assumed fuel efficiency of 0.96 is way too high—the project team should explain the basis for this assumption. The choice of ethanol oxidation catalyst does not make sense. The product of the ethanol oxidation is not clear. There is no way to break the C-C bond at low temperature. The decay rate of 19 µV/h is too high. For the fuel cell decay rate, 3 µV/h is normally acceptable. DOE has high expectations of talented national laboratory researchers; however, the progress of the project was not too positive.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- The team consists of a good mix of university, national laboratory, and industrial partners. Collaboration with SFC and Oorja Protonics is very advantageous to the team because SFC has expertise in portable DMFC systems and Oorja has expertise in high-power DMFC systems. The team can obtain valuable information on the material/performance requirements for portable power and high-power DMFC systems.
- There is good collaboration with university, national laboratory, and industry partners. It is nice to see a DMFC developer as part of the team to integrate the MEA into its DMFC system and independently test it and validate the performance.
- There are very good collaboration with industry, national laboratories, and universities as well as with international collaborators; it would be nice to see some more industrial collaborators, now that good power densities are being achieved.
- This project features good collaboration with partners. The involvement of SFC and JMFC is beneficial and ensures that any advancements make the transition to industry.
- The project includes many partners who contribute a wide range of expertise. At times it appeared that the project might be operating as several autonomous units; in future iterations, it may be helpful to include a tighter focus so all partners stay fully engaged.
- The lead PI assembled a great research team. The collaboration with industrial and systems partners such as SFC and Oorja Protonics is an excellent addition. However, the interaction between anode catalysts by each research group needs to be improved because they seem isolated.
- Presently, all institutions are working in their own field of expertise, which leads to good progress in the individual fields. An integration of the individual results, however, is missing. It would be interesting to see a combination of the new membranes with low methanol permeation and the high-activity anode catalysts. Also, the work on DDMEFCs and DEFCs is not connected to the work on DMFCs. For example, the results on DDMEFCs are compared to the results on DMFCs with commercial catalysts only.
- A clear responsibility for each party was not seen.
- There are lots of partners, each focused on its own little box. It is unclear why one of the developed membranes was not used in the performance test. The HFR appears to be too high compared to Nafion® 212. It is unclear why the results were plotted in the bar graphs versus Nafion® 115. A lot of work was done, but the partner interactions were unclear.
- The OEM appears just to have tested one MEA; it is not clear how feedback is working with regard to the importance in performance. It is not clear what is most important, i.e., current efficiency, durability, or peak performance? How were MEA components selected accordingly?

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.4** for its relevance/potential impact.

- The project is relevant to the objectives of FCTO’s MYRDDP. All activities are aligned to DOE’s goal. The focus of the project is on the development of advanced materials, such as catalysts, membranes,

electrodes, and MEAs for DMFC application, and it is expected to fulfill cost, performance, and durability requirements established by DOE. Meeting these requirements is very important for the commercialization of DMFC technology.
- The project is very well matched to DOE and FCTO goals for portable power. It addresses the critical limitations that are holding back widespread adoption of fuel cells for portable power. The progress from the project has been mostly incremental, but it is real and important.
- The project objectives are in line with the DOE Hydrogen and Fuel Cells Program (the Program); more specifically, the project addressed key issues in direct methanol and other liquid-fuel-based fuel cells for portable applications.
- Fuel cells with liquid fuel are ideal for portable applications. The research toward this application is a must.
- This project covers all aspects of DOE's goals for portable fuel cells.
- The work on DMFC and DDMEFC, focusing on highly active catalysts and membranes with low crossover, is highly relevant to achieving DOE goals. The relevance of the DEFC work will depend on achieving a stable catalyst with a high selectivity for the 12-electron process as proposed in the future work.
- It is not clear how the project is going to achieve the system cost target of $3/W. The catalyst loading is still relatively high. The performance target is a system target—it is unclear whether this is taken into consideration when determining the project's progress toward this target. It is unclear whether certain assumptions about the system (e.g., BOP, power controls, and fueling container) are made to calculate the performance target for the project, and, if so, what the assumptions are. The project is more research and development focused, with an emphasis on advanced materials development; therefore, system considerations are likely not taken into consideration. The durability of the advanced materials in a system is relevant and important. The path to large-scale fabrication of successful materials is a good objective.
- DMFC catalyst loadings are very high compared to hydrogen fuel cells, and power densities of the fuel cells are much lower. It is not clear how DMFC, DEFC, or DMEFCs help DOE reach its overall goals of reducing petroleum imports and CO_2 emissions. The costs are high due to the high PGM loadings needed and low power densities, and these fuel cell systems are unlikely to move into anything other than niche applications where impacts on petroleum usage and emissions will be negligible. In addition, the technology is sufficiently different that their adoption will not significantly impact production volumes for hydrogen fuel cell materials or impact costs. The potential benefit is getting users familiar with fuel cells, but this is a limited benefit.
- DOE made great efforts to promote fuel cells and hydrogen; however, every year, good stories always come from national laboratories without any promising applications.
- There appears to be poor correlation between DOE goals for portable power and project goals. LANL was criticized last year for not considering DME systems, and that pattern continues this year. Just optimizing the catalyst for these systems does not answer system questions—the OEM partner should be able to help here.

Question 5: Proposed future work

This project was rated **3.1** for its proposed future work.

- The future work described is aligned with the proposed work of the project.
- The proposed work plan is a reasonable extension of the existing work. Because this project is near the end, some practical metrics need to be addressed: the scalability of the new catalysts and membranes, cost/performance analysis, etc. The viability of the BNL catalysts needs to be demonstrated on at least the MEA level in a real fuel cell.
- In general, the proposed future work is good. It is recommended that the PI examine a higher concentration of fuel and/or develop a membrane that lowers methanol/fuel crossover. The PI should focus on testing lower catalyst loading and on developing a new catalyst that is non-PGM, if possible, to lower costs.
- Future DMFC work is focused on further increasing the cell voltage, on catalyst stability, and on demonstrating a 500 W DMFC system with reduced catalyst loading. This will make the DMFC results suitable for industrial application. Further work on catalysts and implementation of multiblock copolymer membranes will lift the DDMEFC to a level the DMFC has already reached. DME crossover studies are

suggested and should be compared to similar studies on DMFCs. For DEMCs, the proposed work on catalyst stability and 12-electron selectivity is crucial for the usability in a real-world cell.

- The PI has identified critical issues and a realistic path to success in methanol, DME, and ethanol work.
- The project has almost ended so there is relatively little proposed future work. That which is proposed is sensible and appropriate.
- LANL is approaching four years on the project and is still looking at new materials; this part of the project should certainly be demonstrating long-term durability, relevance to system targets, and cost analysis.
- Ethanol oxidation may be premature. It is suggested that the PI first get the methanol and DME to work properly. Integration of the developed components into a functioning MEA (the nanowires/AAC/membrane) also shows better partner collaboration.
- This reviewer does not believe this project will have value for industrial applications.
- The project is scheduled to end this fiscal year.

Project strengths:

- The team is well organized and capable of developing DMFC membranes and MEAs. The team is composed of respectable research organizations with adequate expertise. Overall, the team is equipped with the knowledge base, resources, and industry/academia/national laboratory mix that is required for the success of this project.
- The team is strong and highly capable. Good progress has been made on JMFC DMFC catalysts, LANL DME catalysts, and Virginia Tech hydrocarbon membrane thrusts. The collaboration with industrial and systems partners such as SFC and Oorja Protonics is an excellent addition.
- A strength of this project is the integration of research into catalysis, electrode design, and membrane synthesis.
- Incremental but significant progress has been made on many fronts related to use of liquid alcohol and ether fuels in portable fuel cells.
- The catalyst work is the major strength of this project. The inclusion of industrial partners such as JMFC and SFC is also a strength.
- This project features excellent research by individual partners in their respective fields of expertise.
- This project features strong research capabilities, especially in generating new materials.
- This project features good individual efforts from each partner in its own portion of the project.
- The project’s strength is the team and its expertise.

Project weaknesses:

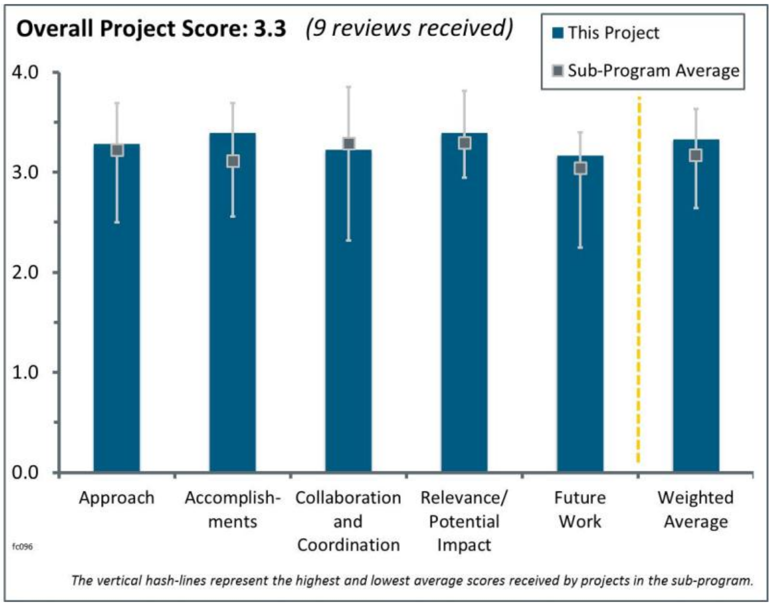
- Project direction is the biggest weakness; there appears to be a lot of work over different areas without much coordination or steady progression toward Program goals. The strength of the team is also its weakness—the team members are very good at generating new materials and have spent most of the project resources on this task. As the project progressed, this task should have been narrowed.
- The coordination and interaction between research groups need to be improved because they seem isolated. The catalyst development projects at UDel and BNL need to be gauged against catalysts developed by JMFC and LANL, preferably in actual fuel cells, to help judge their efficacy.
- The project needs more scientific input. Much of this project seems to be empirical. There are no real theories about where to go in terms of catalyst formulation and no ability to screen catalysts for product specificity.
- Project weaknesses include the lack of appearance of partner cooperation, insistence on very high Pt loadings, and possible problems in scale-up of the nanowires to commercial levels.
- A weakness of this project is the combination of a large number of research organizations, which may be a management challenge for the prime organization.
- The project is a bit diffuse, with many parts operating, but not always with great synergy.
- There is limited cooperation between partners.

Recommendations for additions/deletions to project scope:

- It is unclear why so many fuels are included in this project. Improvements in DMFC performance, durability, and reduction in cost are what is needed to bring portable fuel cells to commercialization. Methanol cartridges are already approved for onboard passenger airplanes. Therefore, it is recommended that an ethanol oxidation catalyst not be added to the project because it will be not provide as much power as methanol. Toxicity is the only reason for choosing an alternative fuel to methanol, but methanol toxicity is not an issue for commercialization.
- Because this project is near the end, some practical metrics need to be addressed: the scalability of the new catalysts and membranes, cost/performance analysis, etc. The viability of BNL catalysts needs to be demonstrated on at least the MEA level in a real fuel cell.
- Because the project is finishing up, all efforts on new materials should end and the focus should be on performance, durability, and cost.
- LANL should remove ethanol research from the scope; this is premature to be funded by DOE. The team should also add system integration of all the individually developed components.
- LANL should screen ethanol catalysts for product specificity.

Project # FC-096: Power Generation from an Integrated Biomass Reformer and Solid Oxide Fuel Cell (SBIR Phase III Xlerator Program)

Patricia Irving; InnovaTek, Inc.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Brief Summary of Project:

The 2013/2014 objective of this project is to demonstrate the technical and commercial potential of power generation from an integrated biomass reformer and solid oxide fuel cell (SOFC) for energy production, emissions reduction, and process economics. InnovaTek's steam reforming fuel processing technology has multifuel capability, using natural gas as the bridge to renewable nonfood biomass. Effective thermal integration (with combined heat and power [CHP]) and off-gas recycling enable high system efficiency. Additive manufacturing (three-dimensional [3-D] printing) is used to reduce the fuel processor equipment cost.

Question 1: Approach to performing the work

This project was rated **3.3** for its approach.

- The project clearly defines the barriers and how it plans to overcome those barriers. There is excellent integration with the Mid-Columbia Energy Initiative. The project has a logical flow that clearly documents the successes throughout.
- The project seems to be going well. The researchers have achieved an impressive reduction in size and part count for the fuel processor.
- The approach is very good—adding multifuel capability makes a lot of sense.
- This is a great project. It is well planned and executed with a laser-like focus.
- The project was well designed, feasible, and well integrated with other efforts.
- It addresses cost, performance, and durability for small distributed generation systems. The approach is reasonable and direct: develop and demonstrate a fuel cell distributed energy system that operates with second-generation biofuel. Several important aspects of the approach are as follows:
    - Use of a system based on InnovaTek's steam reforming process and SOFC (major emphasis).
    - Nonfood biofuels that include pyrolysis oil and bio-kerosene processed locally.
    - System to be demonstrated in Richland's renewable energy park and tied to grid.
- The project uses biofuel for SOFCs. It is a good concept. The cost of the biofuel is unclear. If the biofuel costs a lot, the whole system can run on natural gas and other fuels.
- The project addresses the burner system but no references were listed for S impurities. This could be critical. The sulfur scrubber was shown in the process flow diagram, but not much information was presented on it.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.4** for its accomplishments and progress.

- The incremental improvements of the system design and overall simplification of the system are excellent. The use of additive manufacturing for the innovative components pushes the technology further than expected. Performance gains of the system are very close to DOE targets and above many other systems targeting similar applications.

- The project seems to be on track to achieving all or most of its goals. Impressive results have been achieved thus far, although it is early in the long-term testing. It will be good to see the results of the long-term test. The project is slightly behind on schedule but within reason for a project of this complexity.
- The project achieved its goal of demonstrating the use of reformed biofuels in a fuel cell system.
- The technical results and economic analysis are very sound.
- The cost numbers quoted for the SOFC are outstanding. This unit should be cost comparable if not better than other fuel cell technologies. Even at 1,000 units per year, these numbers are very good; they should be crosschecked with the 5 kW numbers from Battelle.
- The project’s technology has been improved from last year due to the following:
    - Addition of ejectors and nozzles for the reformer.
    - Reduced part count and complexity.
    - Improved stack efficiency.
    - Addition of a heat exchanger for CHP.
    - Production of two gen-3 prototypes.
    - Came close to 2015 goals.
- The project could check the potential lifetime of the system first. Any good system or catalyst without lifetime is useless. DOE should think about lifetime and performance together.
- Laboratory demonstration of the performance and durability is important and not yet clearly presented. Some of the progress from year to year appears to be better than expected and the reviewer is concerned about the reality of this progress.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- This project features excellent collaboration with the following:
    - Subcontractors: Topsoe – SOFC; manufacturing partners – 3-D Printing (Direct Metal Laser Sintering)
    - Strategic partners: Impact Washington – commercialization strategy support; Pacific Northwest National Laboratory – provided upgraded bio-oil made from non-food biomass (within the DOE Hydrogen and Fuel Cells Program); Honeywell UOP – provides bio-kerosene; Systems Integrators – working with several commercialization partners for identified markets; and Mid-Columbia Energy Initiative – collaboration for demonstration.
    - Education: Supported one graduate student from Washington State University and one Delta High School intern in mechanical engineering and chemistry.
- The project seems to be collaborating with partners very well. InnovaTek is supporting students at high schools and universities and collaborating with manufacturers and a national laboratory. The addition of Topsoe fuel cells appears to be good.
- The support for the graduate student and the high school intern was good. The project enjoys excellent partners and collaborators spanning a cross-section of academia, private industry, and potential customers.
- The project has a good range of collaborators—all the way from a stack manufacturer to end users.
- Subcontractors may or may not be providing strategic input to help the project—this is not clearly defined. More involvement from the national laboratory level may be useful with respect to modeling.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.4** for its relevance/potential impact.

- Operating fuel cell systems on biofuels and natural gas and utilizing them for CHP is an excellent nonautomotive application that needs more attention. This project is nearly meeting DOE goals for hydrogen production and CHP.

- The work is very relevant to the Program's research and development goals. Biofuel is a renewable energy with a CO_2 reduction effect, and the work with natural gas is in line with commercializing CHP systems. Completing this project is a way to advance technologies and generate jobs.
- The project aligns well with the Program's and DOE's research, development, and demonstration (RD&D) objectives and has the potential to advance progress toward DOE RD&D goals and objectives.
- The cost and performance values reported by InnovaTek should open the market for CHP and replace the market left by ClearEdge Power.
- The technology developed has great potential and broad and diverse market opportunities.
- Focusing on longer-term renewable fuel sources is important for the DOE mission.
- Biofuel for hydrogen is a good concept; however, the cost is too high.
- While the project was successful in demonstrating the technical feasibility of operating fuel cells on reformed biofuels, there is no business case for it. Thus, the project will have little impact in the real world.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The future work that is right around the corner—the continuation of the long-term performance test—is of great interest. The remaining future work is consistent with, and a natural extension of, the progress to date.
- The integrated system appears to be a technology leader for natural gas. Cost numbers are very good. Performance numbers are excellent.
- The future work is important to providing evidence of performance, durability, and viability.
- The proposed future work is a reasonable and logical continuation; if high-temperature polymer electrolyte membrane (PEM) is a real additional option, it should be evaluated thoroughly. A small phosphoric acid fuel cell might be better.
- The future work, which involves the following, is well planned:
    - Continue long-term performance tests of the fuel processor with both biofuel and natural gas to obtain durability data.
    - Obtain performance data for multiple fuel processors.
    - Integrate balance of plant and the fuel cell.
    - Verify performance and durability with long-term and accelerated stress testing.
    - Further analyze process economics and market strategy.
    - Continue collaborations and establish additional relationships with fuel cell partners and systems integrators for the markets identified.
    - Conduct additional Phase III projects for auxiliary power unit applications with HT-PEM (beyond this project).
- It would be great to see a 1,000 hour test with an integrated system. The team should track CHP efficiency because components lose performance.
- The researchers need to think about the market.

Project strengths:

- First, this was a very well presented project. The slides were awesome. They effectively presented a good picture of the project and were very easy to follow. Well done! This project has been well planned and executed. It is meeting its technical goals. It involves an innovative use of new technologies such as 3-D printing of parts. It is meeting the DOE technical targets.
- Reductions in size and part count are a strength of this project. Additionally, the economic analysis showing estimated costs of $1,722/kW at 50,000 units per year is impressive, and the technology should penetrate the CHP market if long-term testing is successful and these costs are achieved.
- A strength of the project is the incremental improvements in the system design to reduce part count and simplify the system.
- All of the data are very positive. InnovaTek is reporting a very successful project, and performance is much better than polymer electrolyte membrane fuel cells. An electrical efficiency of 42% was demonstrated on reformed fuel.
- This project features solid work with a lot of in-house competence and valuable collaborators.

Project weaknesses:

- There are no weaknesses in this project.
- Challenges remain, but there are no glaring weaknesses in this project.
- There is concern that once this project ends, DOE will not continue working on biofuel fuel cells and reformed fuel systems.
- The long start-up time for SOFCs reduces the market. They are not competitive on a cost of energy basis with natural gas. Only 300 hours of durability performance was demonstrated. Even at 1,000 hours, durability remains an issue.
- More data on durability and start/stop performance would be helpful. The biofuel appears to be a dead end.

Recommendations for additions/deletions to project scope:

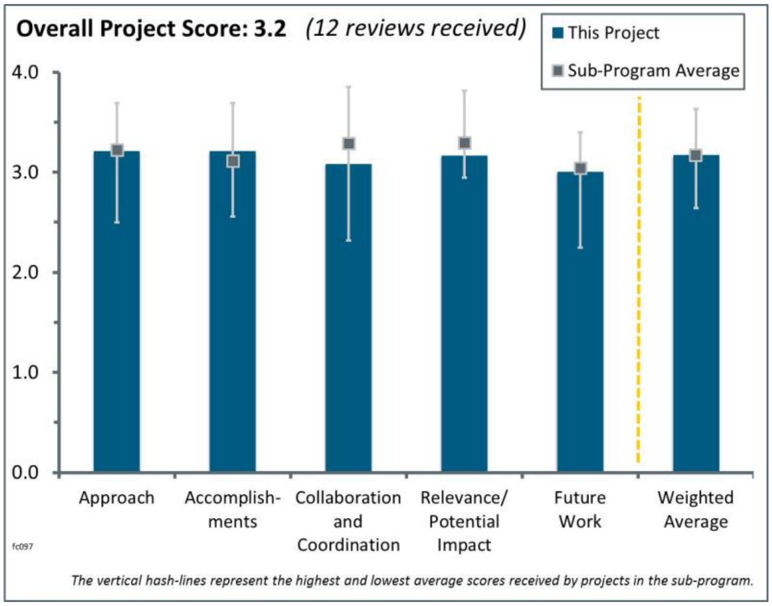
- The data reported by InnovaTek should be used to advance this power system for commercialization. This effort should be moved to the Technical Validation sub-program based on InnovaTek’s reported data.

Project # FC-097: Stationary and Emerging Market Fuel Cell System Cost Analysis—Auxiliary Power Units

Vincent Contini; Battelle

Brief Summary of Project:

This five-year project develops independent models and cost estimates of fuel cell systems for stationary and emerging markets. Goals include: (1) identifying major contributors to fuel cell system component, materials, and manufacturing cost; (2) quantifying potential cost reduction based on technological improvements; (3) identifying areas for manufacturing research and development (R&D) to improve quality and/or throughput; (4) developing a basis for consideration of transition from other industries; and (5) developing accurate cost projections that can be used to evaluate total cost of ownership and facilitate early market adoption.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.2** for its approach.

- This is a well-designed project. The cost estimates seem reasonable. It clearly shows that the balance of plant (BOP) is the cost driver in solid oxide fuel cell (SOFC) systems and why SOFC systems may be unsuited for transportation applications where the heat is wasted.
- The modeling is important to provide a breakdown for status and projections. It would be helpful to know how this project is similar to and different from the sister cost reporting and modeling projections, or perhaps the team could add a collaboration step for status checks of assumptions and results with these similar projects.
- The cost estimate methodologies are logical and appropriate. Key assumptions need to be clearly defined, and comparisons with previous cost estimates are suggested.
- Real-world estimates of cost for components, industry-based design information, and life cycle cost are all critical to a strong understanding of the relevant issues.
- Using the design for manufacture and assembly (DFMA) approach for analysis of a generic fuel cell system design is appropriate methodology.
- The approach is good and thorough.
- This project is broadly focused on cost analyses for both stationary and emerging-market fuel cell systems, with a specific focus on auxiliary power units (APUs) and material handling units. The approach is structured around activities that address three major barriers—cost reduction of fuel cell components and materials, manufacturing capability, and customer acceptance. The approach results in cost estimates derived from detailed models of manufacturing components. For the most part, the activities undertaken address these major barriers. The approach does provide a useful sensitivity analysis to identify significant cost contributors but does not yet address details on the manufacturing sub elements that are major cost contributors. There are also limited efforts to address key uncertainties.
- Analysis starts with a market assessment, which provides a good foundation for system design and costing.
- Initial cost and manufacturing data for the APU application can be obtained from non-U.S. sources that are producing high numbers of SOFC stacks. The data used and system designs represented in this study need

to be updated; Delphi is no longer developing APU systems and changed its design prior to exiting the market.
- The researchers make reasonable estimates for most of the fuel cell system costs. This period, they have focused on SOFCs and performed a cost analysis versus units made. Their conclusions are not very surprising—namely, that materials processing limits cost in SOFCs.
- It is not clear what information is sourced from literature and what—if any—is relevant input from industry.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- The details in the cost estimates for manufacturing analysis are strong and are helping to refine the overall life cycle cost of the systems. While many pieces of data were not readily available, the data presented is reasonable and helps to move the project along and bring it to the group for discussion.
- Excellent progress has been made in estimating SOFC system costs.
- The researchers have made very good progress with regard to both the specific project goals and the broader goals of the DOE Hydrogen and Fuel Cells Program. They have completed the manufacturing model and applied it to the APU case study. The models are currently in Excel format, and it is not clear to what extent the models are available to DOE or other collaborators. There was some brief mention of model validation, but few details were shared on how effective this effort was in establishing model performance goals.
- The results published seemed to satisfy what the project team aimed to do. It would have been helpful to see the similarities and differences of the 1 kW and 5 kW systems. Some of the tables were assumptions/inputs and perhaps more time could have been spent on the results, with the assumptions moved to backup.
- Key findings include the following:
    - Production volume has negligible effect on stack costs.
        - Ceramic material and commodity costs are constant across all volumes.
        - Material processing requirements limit throughput.
    - The Manufacturing Readiness Level (MRL) for many BOP components indicates they are not ready for mass production, and this is a significant cost driver.
        - DMFA performed on specific components (reformer, desulfurizer, and stack) assumes technology with an MRL >9.
- Manufacturing cost analysis was completed for SOFC APUs and polymer electrolyte membrane (PEM) material handling equipment (MHE).
- The team is adequately working toward all its goals. It seems that input from cutting-edge innovations, which might lead to dramatic changes in cost, are not included in the team’s analysis, suggesting an inadequate literature review. Such a review should be included in the future.
- The project should be reviewed by people who actually build similar systems (especially SOFC). For example, it is surprising that insulation was not a top line item. SOFC has multiple very high temperature components, which require expensive refractory insulation. This cost is not trivial. In addition, costs to retrofit the system into a vehicle are substantial—and not shown as a top line item. The learning curve on slide 20 seems off. At a volume of 100 units, items would be built and assembled by hand because tooling costs would be too expensive relative to manual labor. However, at a volume of 50,000 units, tooling would be used. The reviewer would expect the cost differential to be at least threefold, while the cost drops only 1.7 times.
- The MHE PEM analysis of cost is the best database available to the public. A critique from Ballard and Plug Power would be helpful. The costs may be excessive if design dependence on S removal with three expensive heat exchangers after the reformer is assumed. Battelle should review the InnovaTek design, which is simpler. The Battelle 5 kW SOFC system cost is almost twice that of InnovaTek. Battelle should work with InnovaTek.
- It is hard to judge if these results are of real help to manufacturers.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- Excellent collaboration was demonstrated. The following companies provided support for the costing effort:
    - NexTech Materials: System design review/feedback, SOFC technology assessment.
    - Precision Combustion, Inc.: Fuel processing technology review/feedback.
    - Delphi: System design review/feedback, BOP design comments.
    - AVL: System design review and application feedback.
- This reviewer appreciates that collaborators were clearly identified this year.
- Broad collaboration is evident, but more involvement from truck original equipment manufacturers might be beneficial.
- There was only a brief discussion of collaborations, and the presentation did not provide much detail on these collaborations. There was limited discussion of what value was added as a result of the collaborations. In particular, there could be more effort to use collaborations with manufacturers to get better insight on the likely ranges of parameters used to model manufacturing processes, as well as collaborations with other national laboratories to have consistency in the metrics used for life cycle cost.
- The researchers should add international partners with a well-defined and accurate manufacturing plan in place.
- Battelle should expand cooperation to include InnovaTek. DOE should facilitate the collaboration.
- Collaboration should be intensified and extended to more partners.
- Additional developers would strengthen this project by providing additional input.
- Input from developers of stationary SOFCs (in addition to Delphi and NexTech) are desirable.
- The collaborators might not be the optimal. For example, Precision Combustion, Inc. is not a mainstream catalyst supplier. While Precision Combustion, Inc. has an interesting product, automotive-style catalysts should be considered (e.g., SudChemie). Such catalysts are canned and toughened for automotive applications already. NexTech materials might also be a bit far upstream to consider for a system-level analysis. The researchers should bring in companies that are leading similar system integrations. Delphi's level of involvement and quality of interaction were unclear.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- This project provides background information, telling DOE whether the efforts on the development of fuel cells are working toward a commercial, energy-saving, and low-pollution product.
- This is important for DOE's status and progress related to fuel cell system costs.
- The project is well targeted and beneficial to the research goals of the Program. The relevance of this work to DOE goals could be improved with more focus on the impacts of assumptions about manufacturing on cost results and with more attention to time frame in presenting life cycle cost estimates.
- The work is addressing technical barriers that are important to the Program:
    - Cost reduction of fuel cell components and materials.
        - Identify major contributors to fuel cell system cost.
        - Quantify potential cost reduction based on technological improvements.
    - Manufacturing capability.
        - Identify major contributors to fuel cell system manufacturing costs.
        - Identify areas for manufacturing R&D to improve quality and/or throughput.
        - Provide basis for consideration of the transition from other industries.
    - Customer acceptance.
        - Develop accurate cost projections that can be used to evaluate total cost of ownership and facilitate early market adoption.
- Impacts of BOP components on SOFC system costs have been identified.

- This is potentially a great market for early adoption of SOFC systems.
- Cost analysis offers insight into important high-component-cost R&D areas and market potential.
- The elaborated cost projections give some indication of costs; whether they are really useful is not clear.
- In a negative way, this honest and fact-based assessment shows what does not work for transportation.
- There appears to be little work outside of the hydrogen focus for the DOE Fuel Cell Technologies Office; this project is very important to meeting the goals for nonautomotive applications. This project can help strengthen this area with a little more refinement.
- It is difficult to assess the impact of this project because the conclusions are somewhat obvious. The analysis was neither terribly exhaustive nor insightful.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The future work holds promise because the lessons learned from the earlier project periods are planned to be expanded into many more different technologies.
- The focus for the next budget period turns to primary power and combined heat and power (CHP) from 1 kW to 25 kW for appropriate fuel cell types.
- The future work is focused appropriately on primary power and CHP applications (e.g., polymer electrolyte membrane fuel cells [PEMFCs], high-temperature PEMFCs, and SOFCs).
- The researchers have organized the work to meet the project goals in a sequential and logical manner. During the next budget period, they will focus on primary power and CHP applications. In planning their future work, it will be important to address an analysis of the sensitivity of cost analyses to assumptions about manufacturing and to consider appropriate time scales for cost estimate comparisons.
- Continuing to refine the work and move onto CHP applications is important to meeting the DOE goals. Systems from NexTech and Precision Combustion, Inc. are both capable of operation on ultra-low sulfur diesel without S removal. The reviewer is curious about what impact removing S cleanup, heat exchangers, and the material associated with that new process flow has on the total system cost and maintenance.
- The proposed work could be done, but it would be better to solidify the results obtained so far to come to viable judgments.
- PEMFCs have been proven repeatedly as being impractical and uneconomical for CHP. There is a long road scattered with the bones of those who have trekked it. Japan still has some activity, which is highly subsidized, and the heating systems applied in Japan are different than the United States. This reviewer has experience with PEMFCs and HT-PEMFCs as a systems engineer. The focus on SOFC may be prudent—especially for larger systems (100 kW and larger). Heat recovery ability has not been clearly demonstrated for such systems, and work to produce such benefits may be of benefit for the Program.
- Questions remain about the validity of the HT PEM, whether someone is taking ClearEdge Power’s place, and whether the HT PEM actually works.
- A more detailed description of the future work is recommended.

Project strengths:

- The researchers are very effective in both meeting their project goals and providing results that are relevant to Program goals. Overall, the life cycle cost and sensitivity analysis is good. The determination and discussion of dominant cost drivers is useful and informative.
- This project features excellent detail and data gathering to develop the system models and start the costing process. There are good collaborations that will help the project if the partners stay engaged.
- This project is well planned and is producing interesting results. It clearly shows that the basic fuel cell stack is no longer the cost driver. The research community needs to go after BOP.
- Strengths of this project are its extensive industry contacts in the United States and rich experience in cost analysis.
- The cost estimation methodologies are a strength of this project.

Project weaknesses:

- No weaknesses can be identified.
- A project weakness is the apparent lack of coordination or comparison with similar DOE cost modeling projects. This is not to say this is not a relevant project in all the DOE cost modeling projects; it would be helpful to know more about how this project supports the DOE cost reporting mission with the other projects. Adding additional partners would be important to get more than one data point for a category.
- It is not clear that there are any collaborators who are currently or will be manufacturing the units being analyzed. The cost of ownership analysis was fixed to three years. Results in the cost comparison table may be quite sensitive to this and other assumptions.
- It was not evident that Battelle has actual experience in manufacturing components for fuel cell systems. The project is dependent on interviews with industry; it is unclear what will happen if industry says no to interviews.
- The project needs a better system analysis; this current design is outdated and inefficient. The researchers should collect data from foreign SOFC manufacturers.
- It is early in the process—the researchers need to add CHP and primary power.
- The work as presented seems to be a bit “hypothetical,” with little relevance to the “real world.”
- There is a lack of certain details (e.g., assumptions and rationales).

Recommendations for additions/deletions to project scope:

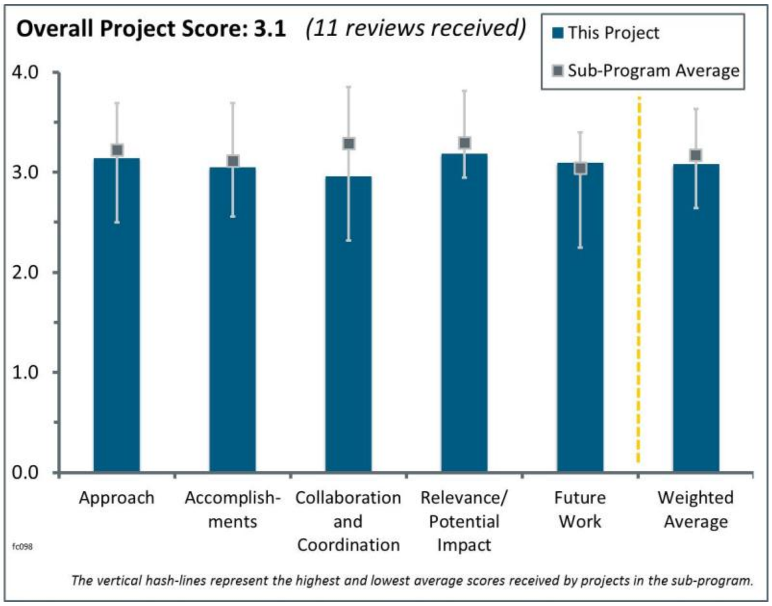
- There should be more efforts to determine sensitivity model results for the cost to manufacture methods choices. The team should work to address model quality control and quality assurance. It should also include more details on manufacturing sub elements—an effort that will be important for overall sensitivity analysis.
- The researchers should pursue more collaboration to achieve more relevant information, which will lead to more realistic results.
- The team should delete HT PEM and add collaboration with InnovaTek for 5 kW SOFC cost analysis.
- The team should make sure end users are involved.
- Comparison with previous cost estimates is strongly recommended.

Project # FC-098: A Total Cost of Ownership Model for Design and Manufacturing Optimization of Fuel Cells in Stationary and Emerging Market Applications

Max Wei; Lawrence Berkeley National Laboratory

Brief Summary of Project:

This project develops a total-cost-of-ownership (TCO) modeling tool for the design and manufacturing of fuel cells in stationary and materials handling systems in emerging markets. The framework has been expanded to include life cycle analysis (LCA) and possible ancillary financial benefits, including carbon credits, health/environmental externalities, end-of-life recycling, and reduced costs for building operation. System designs are identified that meet the lowest manufacturing cost and TCO goals as a function of application requirements, power capacity, and production volume.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.1** for its approach.

- This is a well-established and good process for system evaluation. This project presents a detailed cost analysis that identifies key contributors to cost and determines realistic process-based costs. The project considers realistic production rates for combined heat and power (CHP) systems. Progress to date has been very good.
- The general objective of the project is of great interest to promote the commercialization of fuel cells. Actually, end users need information on the technical and economic viability of the fuel cell technology. The proposed approach—including the design for manufacturing and assembly (DFMA) analysis cost model and integrated LCA impacts, including life cycle costs, carbon credits, and health and environmental benefits—is correct.
- The project features a good approach and detailed investigations. It is a good complement to the work of Strategic Analysis, Inc. (SA).
- Addressing the monetized impacts of health and environmental impacts gives a much better appreciation for how closely the fuel cell systems compete with the grid. It would be interesting to see how the latest U.S. Environmental Protection Agency rulings will impact the grid levelized cost of energy (LCOE). These additional costs will be good for fuel cells. In addition, perhaps demand charges should be addressed—these can be considerable.
- Incorporating other models to minimize redundant modeling work demonstrates good collaboration.
- The approach is good.
- The work approach is designed to address fuel cell costs: expansion of the cost envelope to TCO, including full life cycle costs and externalities (Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan technical barrier 3.4.5B).
- The project has been conducted using appropriate estimating methodologies. However, information on key assumptions and the basis for assumptions is lacking.
- The approach used to get data for the manufacturing model is not clear. Cost areas were identified, but it is unclear where or from whom the project gets the cost data. Because industry has reached high production, it is unclear how confident the project team is in the ability of DFMA to yield correct costs.
- The general approach could be explained better. Including environmental and health externalities is insightful.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.0** for its accomplishments and progress.

- The project features a very thorough analysis of the systems and components. The presentation has some great graphs that show the effects of externality components on the LCOE for fuel cells versus grid power.
- The researchers have done a great job of updating and completing the TCO model for low-temperature polymer electrolyte membrane (PEM) CHP systems (e.g., manufacturing cost model, lifecycle cost model, and externality valuation). In particular, monetizing of health and greenhouse gas (GHG) has been done. A direct cost model for a high-temperature PEM CHP system has also been realized; however, the reliability of the study is unclear because today neither HT-PEM vendors nor a stabilized technology exist, as performance and durability have to be strongly improved.
- The team completed detailed design plans and a bill-of materials and balance-of-plant (BOP) inventory for HT-PEM systems in co-generation and stationary power applications.
- The project features valuable results; the sensitivity analyses for manufacturing volume are very good.
- Progress was presented over a broad spectrum of fuel cell types and applications. The cost breakdown provides insight into research and development (R&D) needs.
- Progress has been made on estimating costs for LT and HT systems.
- The analysis or its articulation could be more consistent. For example, power electronics are spelled out for LT-PEM, but not for HT-PEM. It is also unclear if the backup power systems are alternating current or direct current, or if they have power electronics at all. There are also questions about whether hydrogen storage is present and the number of hours of operation for the systems—those assumptions need to be provided. It is strange that externalities are monetized. The reviewer was unaware of such mechanisms, other than sporadic incentives from different states. This may not be relevant in the analysis.
- For some of the CHP costs, it was unclear what was new and what was a repeat from last year. Take-aways on all the accomplishment slides would have been helpful in the review. The charts set at 100% (e.g., slide 15) were interesting to study how the different segments changed with production volume.
- SA is using DFMA—it is unclear what other technique Lawrence Berkeley National Laboratory (LBNL) could use to estimate higher production cost. SA started before LBNL, so it is unclear why DOE would have the method used by both teams. Perhaps DOE wanted the teams to crosscheck each other.
- Dependence on the grid for load following does not seem like a reasonable assumption. The project would be well served to add energy storage into the system.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.0** for its collaboration and coordination.

- The project features a good cross-section of national laboratories and private industry. The leveraging of other models was effective, particularly for health and environmental costs.
- This project features good advising partnerships, including with the University of California, Berkeley; Ballard Power Systems; and Altergy Systems.
- There seems to be improvement in the area of partnerships and collaboration from previous years. Continued efforts to try to get information from key stakeholders are encouraged.
- The collaboration is correct, but it should be expanded to other end users and system providers. Coordination with the other principal investigator conducting the DOE projects dealing with cost estimation might be helpful for the community.
- Each scenario should have more collaboration from stack integrators and end users with current, firsthand knowledge of component costs.
- Formal collaboration could be expanded to more partners; the informal contacts are very good.
- Additional collaborations would strengthen this project.
- More inputs from fuel cell developers are desirable.
- Only Ballard was consulted; it has very limited experience with systems integration, especially considering that the majority of this work is on CHP systems.
- It is unclear who the collaborator is for the polybenzimidazole (PBI) membranes.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The project fully supports the goals of the DOE Hydrogen and Fuel Cells Program. The significance of the project will be high because the project delivers publicly available, unbiased data, which is important for economic considerations and decisions of suppliers.
- This reviewer concurs with the expanded framework to include LCA. Ancillary financial benefits are very relevant in lowering the TCO and should be addressed in other projects that address TCO and capital expenditures (CAPEX).
- The project aligns well with the Program's and DOE's research, development, and demonstration (RD&D) objectives and has the potential to advance progress toward DOE RD&D goals and objectives.
- The project is complementing the work from SA and leads to more trust in the results for both projects.
- The cost analysis provides some guidance to R&D needs for cost reduction.
- This project is relevant to support DOE's objective of cost reporting and projections.
- The potential impact may be high because it might convince end users to buy and install fuel cell systems. However, the relevance to study the HT-PEM system, which is not ready for commercialization, is not clear.
- The impacts of BOP components have been identified.
- It is important to keep an eye on the state of the technology and its implication on potential system designs. However, it may be prudent to be frugal on technologies that have technical (not cost) challenges—namely, CHP—as LT-PEM systems have consistently been proven inadequate for heating purposes. The emphasis on this system type should be reduced.
- It is important to generate cost information and TCO. The impact may be low because of ongoing work by the National Renewable Energy Laboratory and SA.

Question 5: Proposed future work

This project was rated **3.1** for its proposed future work.

- The future work is properly focused on the go/no-go decision to see if the TCO model is satisfactorily completed for HT-PEM systems in CHP and stationary power applications.
- The proposed future work is in line with the Program and appropriate for this project.
- The proposed future work is a logical, straightforward continuation of the project.
- The proposed plan is correct, except for the continuation of the HT-PEM study. The associated resources should be put into solid oxide fuel cell (SOFC) modeling and into updating the LT-PEM model.
- There seems to be a large difference (by a factor of 5 or so) between LBNL's cost projections and those developed by SA. The future work should address this difference and account for it in terms of different assumptions, different methodologies, etc.
- The future work addresses some of this reviewer's concerns.
- A more detailed description of the future work is recommended.
- It is unclear why HT PEM is emphasized. It is not clear whether it really works or whether it is an expensive replacement for SiC in phosphoric acid fuel cells (PAFCs). The researchers should work with InnovaTek on SOFCs.

Project strengths:

- The model takes into account the total installed system, unlike the automotive systems. It also takes into account health and GHG impacts.
- Project strengths include the creation of publicly available, unbiased cost data, as well as coordination between industry, national laboratories, and consulting companies.
- The project features a very detailed capture of the system components and cost information. The analysis and resulting graphs were easy to understand and informative.

- This project is important for supporting DOE's objectives for fuel cell cost reporting.
- The estimation methodologies are a strength of this project.
- The determination of cost as a function of volume is very good.
- The project features experience in fuel cells from an academic viewpoint. There is no industrial experience.

Project weaknesses:

- The project does not do enough to make a connection between its cost estimates and the costs from actual fuel cell manufacturers. The community would like to see the cost estimates extended to lower manufacturing volumes and compared with actual, real-world fuel cell prices.
- There is a lack of HT-PEM vendors, and the technology is not ready for deployment (lifetime and performance). It is therefore difficult to see the added value of this study.
- It is hard to cover all aspects of this detailed cost analysis in a short presentation. A better job of explaining the assumptions would be useful.
- This project would be helped by having more coordination/comparison with the other projects that support DOE's cost reporting objectives.
- This project is repeating the DFMA of SA; the researchers should develop a new method. There is no industrial experience. The researchers need to depend on industry giving them the cost data.
- The project team has been able to determine with the methodology that CHP can meet the 2015 target at 10,000 systems per year.
- The lack of the full array of technical collaborators is a weakness of this project.
- A wider range of collaborators would be nice.
- There is a lack of information on the basis for assumptions.

Recommendations for additions/deletions to project scope:

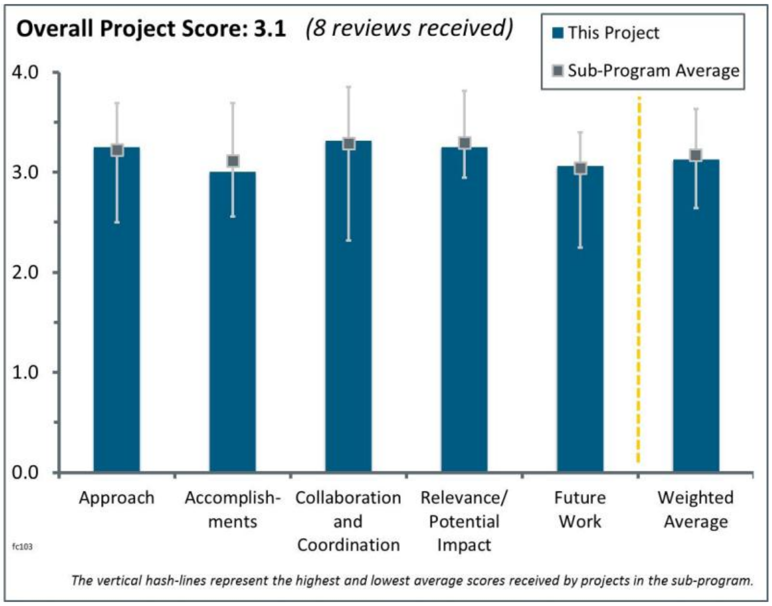
- The researchers should not put a lot of effort into HT PEM, because the technology is not ready. They should also ensure that the cost assumptions among the different cost analyses are consistent (e.g., FC-018, FC-083, FC-097, and FC-098).
- In addition to the capture of ancillary costs, it would be interesting to research the various federal and state tax incentives—such as renewable identification number credits, accelerated depreciation, and peak demand charges—and determine their effect on CAPEX and LCOE.
- The work needs more statistics so confidence levels can be established. There is a lack of HT-PEM vendors and original equipment manufacturer contacts, but the team has started discussions with Advent Technologies and PAFC contacts.
- The team should eliminate the HT-PEM effort until some industry entity makes it work. The team should also find an alternative to DFMA.
- The researchers might consider a detailed cost analysis of high-impact BOP components.
- A comparison with previous cost estimates is strongly recommended.

Project # FC-103: Roots Air Management System with Integrated Expander

Dale Stretch; Eaton Corporation

Brief Summary of Project:

The primary objective of this project is to demonstrate key improvements to compressor/expander efficiency, including compressor/expander efficiency at 25% flow, combined motor/controller efficiency at full flow, and compressor/expander input power at full flow. Secondary objectives include conducting a cost reduction analysis and fully testing and validating air management system hardware capable of meeting project targets.



Question 1: Approach to performing the work

This project was rated **3.3** for its approach.

- The approach is excellent because it incorporates upfront analytical work to improve the device-critical parameters before a concept is down-selected. In addition, the project includes both performance validation testing and endurance testing in an application.
- The general approach of applying computational fluid dynamics (CFD) to guide the design of the expander/compressor and an integrated motor, followed by subsystem integration validation and full 80 kW system validation, is sound.
- There are clear goals with well-defined primary and secondary objectives. The barriers are accurate and clearly presented.
- This project features good and clear approaches based on a real-world problem/issue.
- The approach is good. This project will overcome cost and reliability barriers by leveraging recent advancements to further develop the Roots blower by accomplishing the following:
    - Leveraging the broad efficiency map of Eaton’s Twin Vortices Series (TVS) compressor to improve the overall drive-cycle fuel economy.
    - Integrating the expander, compressor, and motor to reduce system cost and increase system efficiency (this is a new approach, similar to a traditional turbocharger).
    - Reducing part count, and thus cost, by incorporating overhung expander and motor rotors such that four bearings and two shafts are used.
    - Operating at a lower speed to leverage lower-cost bearings and improve system reliability.
    - Developing a net shape plastic expander to lower manufacturing costs.
- The project features an alternative approach to the compressor, eliminating the turndown weakness of air bearings.
- The project features a relevant approach with a somewhat known process map optimized for a fuel cell component. Cost remains an issue, and there does not appear to be much further opportunity to reduce the component cost to the target.
- The approach is classical analysis, design, build, and test. For the most part, it looks as if Eaton is selecting existing subcomponents and assembling them into a compressor/expander module. There seems to be little innovation.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.0** for its accomplishments and progress.

- Compressor and expander CFD work has been impressive. Work in analyzing tip clearance and improving fidelity is impressive. Seven compressor studies and 10 expander geometries provide excellent data and demonstrate clear understanding of how to achieve performance and meet DOE goals at the system level.
- Kettering University's progress is highly relevant and shows good progress with respect to overall project progress.
- The team has made good progress on its goals. The go/no-go metrics are not clear. DOE approved of the project moving forward even though some of the targets are not met by the proposed solution. It would be useful to see the trade-off analysis on the critical parameters and understand why specific decisions were made.
- Eaton has made the following good progress:
    - CFD modeling: Eaton has made strides in modeling three- and four-lobe Roots expanders and compressors. A tool was used to optimize designs.
    - Expander plastic rotor: Plastic rotor hardware has been successfully demonstrated through testing.
    - Develop compressor/expander with integrated motor: Improvements have been made to the expander and compressor design. Compressor/expander matching has been improved as well. The design has been completed, with detailing in process.
    - Hardware procurement: The Ballard Fuel Cell Module Test Specifications, Procedures, and Acceptance Criteria were defined, and a purchase order was issued. Some hardware was ordered.
- Applying STAR-CCM+ enabled a 50% improvement in modeling tip clearances. However, this implies that the modeled tip clearances are still 3.5 times greater than production clearances. The reviewer wonders whether this is a limitation to using CFD to guide compressor/expander design. The reviewer also wonders whether the use of "special software" that can handle production clearances is computationally efficient and viable for exploring a wide variety of design options. It is stated "to improve the expander flow performance, clearances have to be tightly controlled." It is unclear what the absolute dimensions of these clearances are, and whether they can be reasonably maintained with lower-cost plastic components. Also relative to tip clearances, it is unclear whether the effect of thermal expansion has been accounted for over the entire range of expected operating temperatures.
- The progress toward building and testing is okay. Slide 3's projected performance status does not meet some key efficiency targets. Some originally proposed concepts have been abandoned, such as common shafts, and it is not clear whether plastic molding will be successful. Design and build tasks are on track.
- It is too early to tell if Eaton's compressor/expander design is working. The costs are high and similar to commercial turbochargers.
- According to the summary slides, some elements of the project, such as cost, are quite far from the target values. The future work does not quite explain how to achieve the targets.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The amount of collaboration is great, and it is in the correct areas, from the analytical modeling work to the final product testing.
- There is good support from Kettering University. The project partners are highly relevant to both furthering technical understanding and gathering original equipment manufacturer experience.
- The project has a good collaboration team.
- The project features fairly reasonable collaborations.
- Collaboration areas include systems and cost analyses, CFD, and a stack/system integrator.
- The upstream partnerships (subsystem and system level) are strong, but the project could benefit from a motor/controller partner because these components seem to be the primary barriers to meeting the cost target.

- Collaboration is evident; however, all listed entities are subcontractors. It is unclear whether there are any relationships developed for mutual benefit, and whether that is an option.
- The prime is Eaton. The subcontractors are Ballard Power Systems, Kettering University, and Electricore, Inc. Technical support is provided by Argonne National Laboratory and Strategic Analysis, Inc.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- The project aligns well with the DOE Hydrogen and Fuel Cells Program and DOE research, development, and demonstration (RD&D) objectives and has the potential to advance progress toward DOE RD&D goals and objectives.
- The project has broad relevance to balance-of-plant (BOP) components and the long-term durability of the fuel cell stack/system.
- There is good progress toward the goals, and more emphasis on BOP equipment is needed; so it is great to see this project supported by DOE. It is not clear how the proposed technology plans to achieve the DOE targets.
- BOP components are responsible for a significant portion of costs and for most system failures.
- Compressor/expander performance is essential to meeting the DOE targets for system performance.
- If successful, the project should have an important impact. There is not enough data yet.
- There are many projects focused on fuel cell catalyst/support material, membrane electrode assemblies, and stacks. However, fuel-cell-focused component development is very important for successfully launching new fuel cell electric vehicles.
- The project needs more focus on the motor to achieve the efficiency and cost targets. Although the work on low-cost plastic components is important, it was stated in the presentation that the total cost impact of plastic versus aluminum is small.

Question 5: Proposed future work

This project was rated **3.1** for its proposed future work.

- The project has a good plan to perform the endurance validation testing for one year with a partner. This plan could be improved to include additional validation testing under simulated conditions at Eaton that would expand the learning with multiple test units. In addition, accelerated testing should be considered in order to determine any potential failure modes quicker and possibly mitigate them before the end of the project.
- It will be good to see the hardware built and tested to validate models. Integration into a Ballard fuel cell module is also critical to overcoming barriers.
- The project team has done a good job of developing plans for 2014 work:
    - Prototype compressor/expander with integrated motor: Fabricate and qualify prototype components, and determine production cost estimates.
    - Test compressor/expander with integrated motor at Eaton.
    - Undergo project review with DOE, and report progress against go/no-go criteria.
- Testing and evaluation of the integrated air management component (with go/no-go decision), followed by full-system testing and evaluation, seems adequate.
- The project is on the right track for testing.
- The future work entails a continuation of the analysis, design, build, and test progression.
- There do not appear to be any further means of reducing cost or increasing efficiency.

Project strengths:

- Strengths of the project are its strong product knowledge and collaboration with significant fuel cell partners. The academic partner provides solid computational support of in-house testing activities. There is a clear pathway from component development to subsystem evaluation to full system evaluation.
- This project features great collaboration. The project targets an area that needs more development to meet the DOE targets.
- The project excels with CFD models and system configuration and analysis.
- Eaton has a good reputation for BOP components such as compressors.
- This project has a good team.

Project weaknesses:

- The project needs to involve partners/collaborations that provide the skills and knowledge required to close the significant cost gap versus the target.
- The project may need an independent test facility when the compressor prototype is ready.
- The project is not very innovative.
- The project has limited testing.
- The progress seems slow.

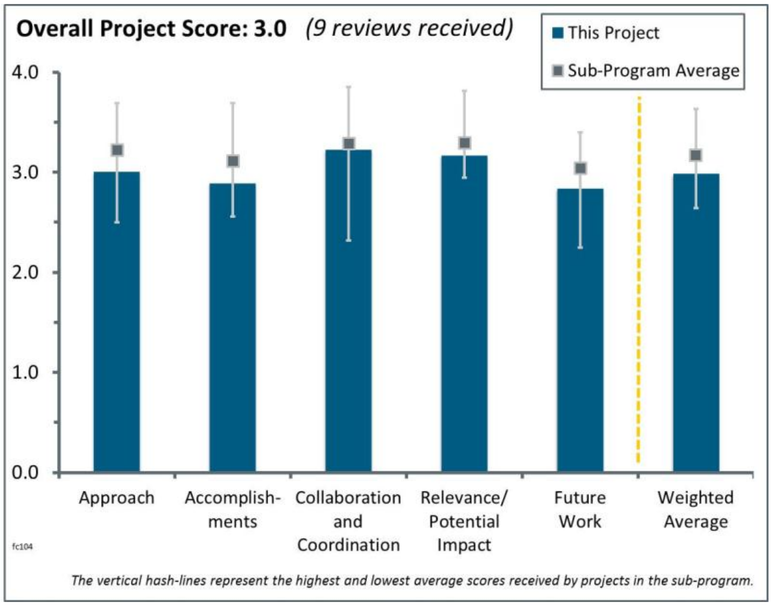
Recommendations for additions/deletions to project scope:

- DOE should support this project.
- The research team may be able to scale back the plastic rotor development work because this does not seem to significantly benefit either the cost or efficiency gaps.

Project # FC-104: High-Performance, Durable, Low-Cost Membrane Electrode Assemblies for Transportation Applications

Andrew Steinbach; 3M

Brief Summary of Project:



This project's overall objective is the development of a durable, low-cost, robust, and high-performance membrane electrode assembly (MEA) for transportation applications that is able to meet or exceed the U.S. Department of Energy (DOE) MEA targets. Primary objectives and approaches this year include: (1) improving MEA robustness for cold start-up and load transients via materials optimization, characterization, and modeling; (2) evaluating candidate MEAs and component durability to identify gaps; (3) improving durability through material optimization and diagnostic studies; (4) improving activity, durability, and rated power of MEAs based on Pt_3Ni_7/nanostructured thin-film (NSTF) cathodes via post-processing optimization and characterization; and (5) integrating MEAs with high activity, rated power, and durability with reduced cost.

Question 1: Approach to performing the work

This project was rated **3.0** for its approach.

- The project is focused on improving the performance of 3M NSTF MEAs in wet conditions and during transients. These MEAs have some of the lowest platinum group metal (PGM) loadings and highest activities demonstrated. Addressing the shortcomings under transient and cold/wet conditions will address key barriers to adoption of this low-loading MEA.
- The approach is to improve the performance and durability of the high-performing NSTF catalysts in MEAs and to integrate the MEAs in fuel cell stack testing. One element of the approach is to improve the MEA robustness for cold start-up and load transient via materials optimization, characterization, and modeling. This is one of the most important and needed aspects of the project.
- The objective of this project is to meet the MEA performance and stability targets, and the approaches to meet these targets are clear. There appears to be a good balance of fundamental studies and operational MEA work to try to elucidate, and counteract, challenges relating to performance and durability. While the objectives are sound, the project seeks to overcome some considerable technical hurdles without making significant changes to the electrocatalyst layers (per the original project plan). In this regard, the scope of work is very ambitious, relying on a finite number of possible parameters to counteract the MEA performance sensitivities.
- The principal investigator (PI) employed a traditional 3M approach that incorporates the NSTF catalyst technology platform. The applied strategy is excellent, and very few details need to be added in order for it to be outstanding. One missing part is the in situ characterization of morphological changes during dealloying and/or during the oxygen reduction reaction (ORR). Considering that J. Erlebacher is a part of the 3M team, the PI should consider utilizing his expertise in understanding the dealloying process.
- The 3M group has set the standard for low-PGM MEA development. The approach for this project is based on further optimizing the NSTF catalysts' platform and initiating testing in short stack with General Motors (GM). The researchers' approach addresses MEA durability, stack material and manufacturing costs, and MEA performance. MEA durability and performance are the focus of the present work.

- The approach is good, considering the constraints of the NSTF catalysts. There has been good effort to perform tests under a range of conditions. The major deficit is that the researchers are bound to the NSTF catalysts, forcing them into certain directions specific to the geometry. The catalysts have typically been prone to flooding at high power, but for some reason this does not show up in the tests. The ORR activity appears to fall off rapidly (see slide 10) by a factor of two over time at 1 A/cm^2. The time is not clear. It seems like the researchers are doing many tests, but perhaps the most relevant is the short stack testing.
- The project addresses DOE barriers related to cost, durability, and performance.
- The Pt/C interlayer is of limited value because there are additional process costs and durability issues with inclusion of such a layer. The approach appears to have a significant chance of meeting cost and performance targets. Although the different anode gas diffusion layer (GDL) designs have demonstrated improvements, MEA temperature performance is still significant and would be difficult to incorporate "as-is" in an automotive application.
- NSTF has serious issues that must be addressed if this novel catalyst architecture is ever going to be adopted as bill of material by any of the polymer electrolyte membrane fuel cell (PEMFC) developers. These issues include its difficulty to break in, high sensitivity to contaminants, extreme sensitivity to low temperatures, and durability. The only way to address these serious issues is to make some serious changes to the electrode configuration. Instead, this project is focused on minor changes that are having only a minor impact. The PI stated that component development is not allowed under the topic for which the project was selected. This reviewer's experience with DOE's Fuel Cell Technologies Office has been that there is considerable flexibility when it is obvious that something different must be done than what was the intent of the original proposal or solicitation. It is highly unfortunate that the PI wants to just continue pursuing work that will not have a major impact.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- There has been a tremendous amount of technical progress and accomplishments—it is almost overwhelming. Almost all of the metrics have been achieved. All of the MEA components were studied using many different and relevant characterization techniques. 3M tested four anode GDLs and down-selected one GDL that has higher water removal capability for MEA integration. The model agreed with the experiments well. It was unclear which of the 4–5 GDL characteristics would have the most impact on cold start-up and water removal; in other words, whether it would be the pore size distribution, contact angle, injection pressure, wetted area (it is unclear if this is measured with water or some other solvent), or thickness that would have the most significant impact, or whether it would be the interaction(s) among the different parameters that have the most impact. This understanding would help one design better GDLs. It is unclear whether the cathode GDL has also been studied for cold start-up, water transport, and transient operation. It is also unclear whether the team plans to use a similar approach to study the effectiveness of the catalyst layer in cold start-up and water transport. An interlayer development was discussed and shown to improve the robustness of the cathode for cold start-up and load transient, but one does not know what this interlayer is and how it improved the performances indicated. Without this knowledge, it would be difficult to design better catalyst layers for this purpose. Factors affecting membrane durability were studied: load cycle temperature, polymer electrolyte membrane (PEM) equivalent weight, and PEM additive. The presenter did not mention what additive or ionomer was used and why these factors resulted in the improvements shown. Also, these fuel cell tests were conducted at higher cell temperatures (80°C, 90°C, and 100°C). It is unclear whether these parameters would have much effect on the cold start-up and transient operations. Annealing and dealloying of NSTF catalysts have shown to improve the mass activity of Pt_3Ni_7/NSTF catalysts.
- Significant progress has been made toward improving anode performance during cold start. Introducing the Pt/C interlayer to address low-temperature steady state and load transient performance does not look like a promising solution. It leads both to an increase in Pt loading and well-known durability problems with carbon supports that NSTF was designed to address. No evidence is provided that performance loss in the presence of the PEM additive is due to anionic contamination. The features in the hydrogen underpotential deposition region before and after the durability tests on slide 58 look almost identical in the presence and

absence of additives in the membrane. The researchers made fast progress in obtaining modeling insights on the effect of GDLs on the performance loss during cold start. Progress toward improving cold-start performance needs to be accelerated in order to start short stack testing next year.

- The PI presented convincing results and confirmed that the thermal annealing protocol is indeed important in improving the catalytic activity (and stability) of NSTF catalysts. As in the past, activity and stability are not an issue for the NSTF catalyst, but water management is still a bottleneck for fully implementing this technology in fuel cell systems. Regarding the active surface area, it is not clear that the project team developed a method that would be able to unambiguously determine the specific surface area of the NSTF catalysts. Rather than using modeling to "capture many experimentally observed trends," it would be very important to see if modeling can be utilized to predict how, or even if, the issue of water management can be overcome in these systems. It is unclear what has been learned from modeling.
- The technical work presented is extremely detailed, and substantial effort is clearly being applied to overcome the challenges of the NSTF layers. These challenges do, however, seem to be increasing in number and relate not only to the known issues of water handling and variable temperature operation, but also to the fundamental activity and stability of the electrocatalyst. Attempts to deal with the latter have offered some success, although it is acknowledged by the PI that these may be insufficient. A range of approaches are being explored to improve the overall performance of the MEA in the diverse range of conditions in which it is required to operate. Clearly, some are proving advantageous, but not to a degree that provides encouragement that the performance targets are attainable.
- The progress is good. The researchers have achieved much advancement with the dealloyed catalysts, although the results are not as striking as those reported by the National Renewable Energy Laboratory and Argonne National Laboratory (ANL). The researchers still need to do a lot more work in order to reach the DOE targets. It was not clear from the data presented if they are on a successful trajectory. Short stack testing is the most critical. The short stack testing is only 10% complete, however.
- The researchers have increased performance at rated power by 60 mV since last year, up to 932 mW/cm^2 (7% increase). They have also decreased PGM total content to 0.138 g/kW and loading to 0.129 mg/cm^2 (12% and 6% decrease since last year). They have moved backwards on performance at 0.8 V while increasing performance at rated power. Load transient operation has been improved. They have met their go/no-go targets for mass activity and high power activity.
- The project team has shown progress in meeting/exceeding the DOE fuel cell goals for catalyst mass activity and durability.
- It would be beneficial to state the bounds of error of the measurements of PGM/cm^2 and potential at high current density as they relate to the go/no-go decision. The researchers made excellent progress on Task 5 toward the targets, as well as in fundamental understanding of exhibited performance.
- To date, this project has focused on "Band-Aids," such as these during the past year:
    - Using different anode GDLs, which have minimal impact because performance is still inadequate at 30°C.
    - Adding complexity and cost such as "interlayers" (the reviewer thought a major advantage of NSTF was supposed to be the elimination of Pt/C.
    - Optimization of the alloy composition (the value is not clear if the electrode is not robust).
    - The PI is changing both the GDL and the catalyst composition, as well as adding an extra layer, which may be perceived as "component development." The reviewer questions why changing the catalyst-layer architecture is not allowed.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- There are good collaborations with Oak Ridge National Laboratory (ORNL) and Johns Hopkins University (JHU), resulting in improved activity through dealloying and improved understanding of structural changes. Collaborations with Lawrence Berkeley National Laboratory (LBNL) and Michigan Technological University (MTU) seem to be leading to improved transient response.
- Good correlation has been observed between the modeling work and experimental tasks relating to the GDL selection, with obvious learning through this collaborative effort. Effect utilization is also evident of ex situ characterization capabilities of the project partners. The interaction with JHU appears to have been

particularly fruitful, with very clear benefits in stability observed by the annealing of the metallic components. The results observed are consistent with those reported in other projects.
- The teaming and collaboration are very strong, involving national laboratories, industry, and universities. The project features a strong team with very relevant capabilities.
- The 3M group has collaborated well with other institutions. The group has worked particularly well with MTU in evaluating water distribution in advanced GDLs.
- The collaboration is good and the partners are well coordinated with the leading PI.
- There is close collaboration with ORNL, MTU, and LBNL
- This project features well-selected partners, good progress, and highly relevant results from partner organizations. A greater emphasis on GM stack data, once available, would be beneficial to understand original equipment manufacturer (OEM) experience with the latest solutions developed under this project.
- The project features a good team, and the members appear to all be used effectively, with the exception of GM.
- Although the list of project “partners” is impressive, the PI does not actually appear to be responsive to the reviewers’ comments. The partners are generally asked to help with 3M’s “Band-Aids,” such as measuring the water permeability of GDLs, instead of actually striving to understand and address the root causes for the major issues with NSTF-based electrodes. For example, if 3M was really interested in taking maximum advantage of collaboration, then results from LBNL’s project on low-temperature sensitivity would be seriously considered and addressed.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The research being led by the 3M group is critical for developing an advanced MEA that can meet the DOE Hydrogen and Fuel Cells Program’s goals. Testing advanced MEAs in hardware developed by system integrators such as GM is an important step to meeting fuel cell system development goals.
- The project has the potential to significantly advance progress toward DOE goals and objectives. The project has significant durability issues to overcome.
- The main cost reduction pathway in this project is reducing the catalyst loading. This is relevant. It is not clear whether there are efforts in reducing the cost of other fuel cell materials and components as well—this would be a good path forward. It would be interesting to see how durable the lower-loading catalysts would be, especially with the contamination issues discussed.
- The project’s potential impact is high, if the robustness and cold-temperature operation of NSTF MEAs can be improved to meet automotive requirements. NSTF MEAs have shown high activity and performance under their optimum conditions, but operational robustness has limited adoption of this technology.
- The project could potentially have a high impact if barriers to performance can be addressed. Addressing performance under load transients, low-temperature operation, and demonstration of some fraction of the reported performance in OEM testing would vastly impact the state-of-the-art PEMFC performance toward DOE goals.
- The development of cathode materials for successful implementation of fuel cells in transportation is of paramount importance. If successful, the NSTF technology may play a key role in the future of alternative energy systems in acidic environments.
- The potential impact of a successful NSTF project has been apparent for some time, and this has not lessened. However, the materials still remain a long way from practical application despite many years of research.
- It is hard to evaluate the impact of the MEAs if they are not broadly available or being tested in a relevant format.
- Unfortunately, after much investment by DOE due to a promising start over a decade ago, it appears that NSTF is becoming irrelevant to the PEMFC community. This does not necessarily have to be the case, but unless serious changes are made, no serious improvements will result and NSTF will not become part of the bill of material for PEMFCs.

Question 5: Proposed future work

This project was rated **2.8** for its proposed future work.

- The project has an effective approach to future work. The key feature is the integration of advanced MEAs into short stacks for testing. Durability would best be assessed in the short stack testing.
- The proposed future work is focused on overcoming performance and durability issues.
- With the short time left on the project, the proposed future work is reasonable and a good path forward. Durability and stack testing of the best-of-class MEA components and low catalyst loading would be most critical (Task 5 and 6).
- The project is scheduled to be completed this fiscal year. The proposed work addresses the key needs to finish the project. The work appears to be more than can be done in the time remaining.
- The proposed future work is reasonable; however, the PI did not demonstrate how feasible it is to expect any further improvement in the development of stable cathode materials and efficient water management.
- The proposed future work is consistent with the project scope and with the outstanding challenges for the project. However, there is little project time remaining to bring into effect the numerous tasks suggested.
- The researchers should develop a root-cause understanding of what causes these major problems (especially relative to Pt/C-based CCMs): difficulty to break in, high sensitivity to contaminants, extreme sensitivity to low temperatures, and durability issues.
- There is clearly a lot of work to be done to get this type of MEA to work. The benefit for the government is unclear.
- If contaminants, etc. are the cause for performance decay, improving activity will not help to increase the performance in MEA applications. The development of recovery methods, although possible as a means of negating lasting performance decay, is not preferred, because of the difficulty of implementation on-vehicle.

Project strengths:

- The project team, which now includes GM, has a strong mix of both research and system development. With 3M spearheading MEA development, the group has made impressive progress toward achieving DOE fuel cell technical targets.
- This project is starting with a high-performing and highly durable cathode catalyst. The project team has shown progress toward DOE targets and since last year. The inclusion of an OEM partner is beneficial to furthering the understanding and observed performance of developed materials.
- A strength of the project is the well-integrated team that can take the information from characterization and basic studies and apply it to improve results.
- The project heavily relies on the previous 3M approach. It is encouraging that the PIs are focusing on the real problem and that they are trying to combine fundamental knowledge with real applications.
- NSTF is a promising catalyst architecture—with many potential benefits—that might be fully realized in a new type of electrode architecture.
- Having a strong modeling team onboard helps to get insights on cold-start performance issues.
- 3M’s expertise in NSTF catalysts and the team are project strengths.
- The continued work on NSTF catalysts is showing slow but steady improvement.

Project weaknesses:

- It appears necessary to take a number of steps outside of the electrocatalyst layers directly (i.e., the substrate choice or use of pressure differentials) to obtain the best performance from NSTF layers, imposing atypical demands of the end user. A number of the challenges appear to relate to the absolute limitations imposed by the material set and that appear unlikely to be overcome with the current electrocatalyst layer structure. The sensitivity of the electrocatalyst layer to the suggested ionomer contaminants is a concern; not least because it suggests the probability of some significant issues in real-world operation in which balance of plant and air contaminants will also come into play.

- Transient conditions and operation at non-ideal temperatures (including start-up) are still issues for the NSTF catalyst. Extra interlayers of Pt/C add complexity and cost to the MEA. The inclusion of a PtNi-type catalyst has issues with respect to Ni leaching and contamination of other stack/system components.
- It is not clear whether 3M is ever going to get to the 2017 goals with the NSTF catalyst structures. The researchers should be doing the hard tests earlier instead of doing tests that emphasize the benefits of their catalysts.
- It seems that the project has too many problems to address. In order to solve one problem, a solution is proposed that brings another problem.
- There are no real breakthroughs with this type of NSTF catalysts. It is disappointing that there is no attempt to develop a new class of materials that may surpass the stability of PtNi-based alloys.
- Although it is out of the scope of research, MEA comparisons using commercially available Nafion® would be beneficial and particularly useful for the durability studies.
- There is a serious lack of root-cause analysis to address major issues.

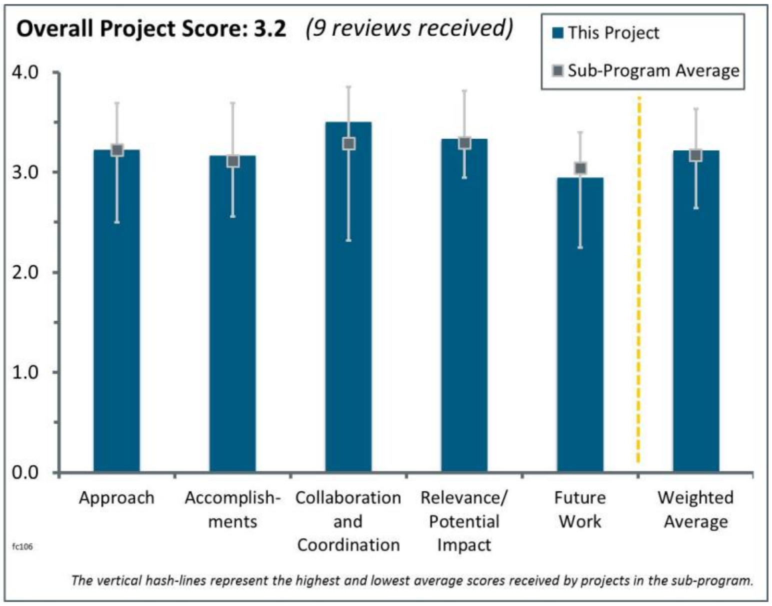
Recommendations for additions/deletions to project scope:

- Catalyst development should be deleted from the project scope. Dealloyed and annealed Pt_3Ni developed by ANL performs well at NSTF support, according to the 2013 DOE Hydrogen and Fuel Cells Program Annual Merit Review report. It was also demonstrated that three Pt monolayers are required in order to protect the alloy core while maintaining high activity.
- Some analysis should be done on the impact of moving water out of the anode on the system and system efficiency. Hydrogen utilization, anode recycling, and purge frequencies during operation may all be impacted, and there should be a check to see if there are negative impacts, and if so, how severe they may be.
- The PI should motivate subcontractors to contribute even more.
- DOE should tell the PI that modification of the catalyst-layer architecture is not only allowed, but required.

Project # FC-106: Rationally Designed Catalyst Layers for Polymer Electrolyte Membrane Fuel Cell Performance Optimization

Deborah Myers; Argonne National Laboratory

Brief Summary of Project:



The overall objective of this project is to realize the oxygen reduction reaction (ORR) mass activity benefits of advanced Pt-based cathode electrocatalysts in membrane electrode assemblies (MEAs) and stacks operating at high current densities and on air and at low platinum group metal (PGM) loading. Objectives in the current year include: (1) determining the catalyst and cathode layer properties responsible for the decline in advanced Pt-based cathode air performance at >1 A/cm², (2) developing a cathode catalyst layer model for an advanced Pt-based catalyst, and (3) developing a method to impart proton conductivity to high-surface-area carbon supports.

Question 1: Approach to performing the work

This project was rated **3.2** for its approach.

- The project focuses on pinning down the structural and morphological properties of dealloyed-PtNi (d-PtNi) cathode layers that limit high current density performance. The team is using extensive in situ, ex situ, and in-cell characterization of electrodes. An excellent experimental design matrix on catalyst inks of 60 compositions is utilized for analytical characterization. The strong modeling effort of mass transport losses complements the characterization results.
- The approach is focused on overcoming performance barriers for advanced catalysts at high current densities. Although modification of the structure of the catalyst layer by changing the ionomer-functionalizing support might help to prevent Ni dissolution in d-PtNi catalysts, it might also create new mass-transport problems related to changing hydrophobic and hydrophilic properties of the catalyst layer. Overall, the approach seems a little bit strange because the structure of the catalyst layer is intended to be drastically changed due to durability problems with the dealloyed catalyst.
- The multidirectional approaches taken by the team for the completion of all tasks are adequate. All the analytical techniques have been thought through appropriately. The study of advanced Pt-based catalyst, developed by Johnson-Matthey Fuel Cells Inc. (JMFC), is a good way to understand the behavior of nanoparticulate catalyst materials under DOE cycling conditions.
- Making a catalyst based on performance-limiting properties appears to be feasible based on the project progress.
- The use of d-PtNi is justified by the fact that it has demonstrated the ability to meet both beginning-of-test and end-of-test mass activity targets for Pt dissolution cycling. The project should be open to other catalysts such as the nanoframe catalysts, mesostructured thin films, and other catalysts with high activity. These catalysts will also need to be integrated into catalyst layers while facilitating high proton conductivity and proper catalyst layer structure. It is good to see that a comparably high-surface-area Pt/C is being used as a baseline. That is the right approach. Characterization of both inks and catalyst layers will be necessary to understand how processing, structure, properties, and performance are all related. There may also need to be characterization of inks and catalyst layers at various stages. It would be good to see whether both wet and dry mapping of catalyst layer components will happen.

- The team has focused on integrating d-PtNi nanoparticles into MEAs, focusing particularly on small, non-porous materials. Fuel cell performance is used as a baseline, which is important, and the team has been focusing on the problems of Ni leaching during use and/or synthesis and its impact. There is no evidence for the team's critical assumption that high current density performance is limited by mass transport through the ionomer. This seems to result from modeling that shows a lower surface area enhancement factor. However, in d-PtNi, it is well known that the hydrogen adsorption is intrinsically smaller (by more than one half) than on Pt, which the researchers show. It would be useful to probe the dealloyed catalysts for surface Ni, which should show up as hydroxide peaks while scanning in base.
- The approach to optimize the cathode catalyst layer specifically for alloy catalysts at low PGM loading does merit some investigation; however, it is unclear whether a detailed investigation of the matter is needed. The approach of modifying the ionomer-to-carbon ratio and the solvent composition in the electrode design has been studied for decades and is more of a development approach than a new idea that could dramatically improve cell performance.
- Gaps to the ultimate targets are not shown. It is not clear what the path is to meet the barriers listed at the beginning of the presentation and whether the project has taken these as targets. The impact table provides the status against targets, but there is a gap because the table contains no high current density targets, whereas the project objective is focused on high current density performance. The durability barrier is not addressed to date, but there has been good work on looking at Ni dissolution. The project has a well-designed approach, with a good balance of fundamental and empirical studies to understand the effects observed, such as the agglomerate size/solvent studies looking at interactions with catalyst type and ionomer concentration, the Ni oxidation effects of solvent concentrations, and modeling approaches. There are good, detailed characterization studies to support the observed effects.
- The reason for the catalyst performance loss at high current densities may already be known based on mass transfer coefficient measurements at low catalyst loadings, non-PGM catalysts' behavior at large current densities, and contaminant effects effectively decreasing active surface area: the decrease in active centers implies a larger oxygen flux and mass transport impact through the ionomer covering the catalyst (slide 27). From that standpoint, the work should be refocused to the design and fabrication of catalyst layer structures that minimize that transport loss. Other approaches should be considered to reduce the risk (e.g., thinner ionomer coating, new catalyst layer structures). The model's usefulness cannot be assessed because no information is provided. The team could use the results of the FC-049 project rather than creating a new model. It is not clear what the stability of the catalyst support proton conductivity (slide 17) is. In addition, it is unclear whether the proposed approaches consider this requirement. Anecdotal evidence from long-term degradation suggests that mass transfer changes in electrodes may be linked to surface functionality modifications. Therefore, the reviewer wonders if it is reasonable to expect stability of the carbon support modifications under long-term conditions.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- Addressing the mass activity loss at high current density of state-of-the-art PtNi electrocatalysts impacts critical limitations of dealloyed catalysts. The composition of PtNi was optimized, which resulted in a highly active catalyst with controlled particle size and the smallest Ni amount. All project milestones were exceeded. The model demonstrated that interaction between the ionomer and the catalyst may be directly related to mass transport losses.
- The team has exceeded the DOE 2020 target for ORR mass activity. The team has also demonstrated minimizing carbon agglomerates through annealing of Pt/C inks. Promising proton conductivity has been demonstrated by functionalized carbon black, which addressed the low performance of SEF catalysts. The mass transport losses related to lower surface area enhancement factors (ECSA/electrode area) of d-PtNi were also demonstrated by modeling.
- Good progress has been made in meeting and exceeding DOE targets for catalyst performance.
- The early milestones have all been exceeded, but they were based on performance improvements only, and the link to the ultimate targets is not shown. Improvements in voltage due to cell compression should not be considered improvements in technology, but rather indicate an improper setting of the baseline. Therefore,

exceeding the goals is not a significant achievement. The project team is wisely resetting the targets; however, the targets should be set with a clear path to ultimate objectives. It is suggested that the researchers set a goal where the expected kinetic benefits of the PtNi are realized at the low current density, and the high performance is maintained out to at least 1.5 A/cm^2 (better than Pt) and also meets >1,000 mW/cm^2 at this current density with <0.125 mg/cm^2 PGM.

- Good progress has been made toward improving the activity of the version 1 dealloyed catalyst, which did not perform well. Not too much progress has been made with respect to improving the durability of the dealloyed catalyst.
- The mass activity of the catalyst exceeds the DOE 2020 target, but voltage loss remains high at high current densities due to high O_2 transport resistance local to the Pt surface. There is no clear path to reduced local resistance.
- It is not clear what is causing the gain in performance observed with successive generations (JMFC results on slide 7). It is unclear if these performance changes are only variations due to manufacturing variability, or whether they are the result of modifications based on a specific hypothesis. This is an important question because confidence needs to be established that these results are reproducible and scalable. An improved catalyst formulation given on slide 8 is an insufficiently clear explanation. It is unclear if the thickness of the ionomer layer covering the catalyst is being measured, because it is expected to play a significant role in the mass transfer loss. For example, the ink solvent may affect the ink rheology and the thickness of the ionomer layer. The other parameters mentioned on slide 9 are not considered as important from a mass transport point of view. From that standpoint, the reviewer wonders if the propanol d-PtNi ink leads to a smaller mass transport loss. Presumably for an equivalent ionomer content, the ionomer film is expected to be thinner, considering the smaller ink particle size and higher surface area (slide 11). It is not clear whether the presence of Nafion® in the ink decreases the free Ni ion concentration by ion exchange favoring Ni dissolution with a lower Nernst potential for Ni (slide 12). The Ni dissolution mechanism of d-PtNi catalysts during cell operation (slide 13) is not clear. The model description is insufficient (slide 14) and does not allow any criticism of the assumptions made. For instance, it is not clear why the anode overpotential is neglected, especially for high current densities, and whether the mass transfer loss correlates with surface activity (slide 16).
- It is difficult to understand how the mass transport losses are associated with the d-PtNi because mass transport losses for it and the annealed Pt are the same. The project team achieved a very interesting result on the lack of ionomer content effect on d-PtNi. Baseline polarizations should begin with optimized compression. Project milestones should preferably begin with the first catalyst (which appears to be the d-PtNi coded “12/409”) and with optimized compression. Sulfonic acid group functionalization of catalyst powders has already been completed and could result in a reduction of ionomer content. This could prove to be important for eliminating a poorly engineered catalyst layer component.
- The accomplishments of this high-quality team are surprisingly poor. The team claims improved cathode electrode performance by an optimization of cell compression; this optimization is needed either because of an initial improper cell design or a behavior that is unique to the alloy catalysts. If it is the latter, a detailed investigation of why alloy catalysts need an optimized cell compression should have been provided. If it is the former, then this performance improvement is simply a cell design improvement and not something that contributes to the fuel cell community. The polarization curve shown on slide 7 looks almost identical to the starting point polarization curve shown on slide 3. The shape is remarkably the same, indicating that no fundamental electrode improvement has been made.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- Collaborations are clearly shown throughout the project. JMFC is heavily engaged in catalyst preparation, ink preparation, and post-mortem characterization. United Technologies Research Center (UTRC) is engaged in cell testing. The University of Texas (UT) is characterizing individual nanoparticles, while Indiana University – Purdue University Indianapolis (IUPUI) is involved in the surface functionalization of catalyst powders. In general, the collaboration appears well coordinated and each partner is more than just a service provider. JMFC, UTRC, UT, and IUPUI all have the ability to heavily influence the project. The project benefits from having a catalyst/MEA supplier involved, JMFC. JMFC should be able to provide feedback about whether new integration techniques for structuring catalyst layers are industrially feasible. The project also benefits from having General Motors (GM) involved as an in-kind partner, to provide cell and gas diffusion layer context. This is particularly true given that some of the targets are related to high current density performance.

- The team consists of a good mix of university, national laboratory, and industrial partners. The collaboration with UTRC and JMFC is advantageous to the team.
- The team interactions and collaborations are very strong. There seems to be good communication and materials transfer between the different groups.
- The results shown in the presentation indicate excellent collaboration among national laboratory, university, and industry partners.
- Good collaboration is demonstrated, with a large number of partners, and the results from a number of partners show the good integration between project members.
- This project features an effective mixture of different organizations with significant experience.
- The project features a very well-coordinated effort between different institutions.
- The project features a strong team involving contributors to all components of the project, including catalyst manufacturing, fabrication and testing of catalyst coated membranes, extensive characterization, and modeling contributions. Purdue University does not seem to fit into the project at this stage.
- Collaboration with the partners could be improved. The carbon surface treatment by IUPUI, although successful, never made it any further. It is unclear whether it improves the alloy performance in a fuel cell.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- Achieving high mass activity of advanced Pt electrocatalysts at high current density is of great significance to the commercialization of these materials. This project brings in fundamental understanding of limiting factors in dealloyed Pt catalysts through extensive characterization, modeling, and testing. Determining the interaction between ionomer and catalyst and its potential link to mass transport losses is a first step toward developing strategies for addressing activity loss at high current density.
- The project is relevant to the objectives of the DOE Fuel Cell Technologies Office’s Multi-Year Research, Development, and Demonstration Plan. All activities are aligned with DOE’s goal. The focus of the project is to realize the ORR mass activity benefits of advanced Pt-based cathode electrocatalysts in MEAs and stacks operating at high current densities and on air and at low PGM loading (≤ 0.1 mg Pt/cm^2 on cathode).
- The project is well aligned with DOE Hydrogen and Fuel Cell Program (the Program) goals and with the need to achieve high performance at high current density with low Pt loadings and for alloy catalysts. The approach of detailed characterization studies, empirical studies, and modeling should lead to significant improvement in understanding and the ability to design optimized structures.
- Focusing on improving performance at high current densities, the project will impact low-Pt-loaded catalyst layer fabrication that could facilitate cell cost reduction.
- High-performance and durable catalysts are essential.
- While it seems clear that dealloyed catalysts will play an important role in next-generation catalyst materials, it is unclear whether this team’s approach has advantages over other approaches (e.g., 3M nanostructured thin film). It would have been useful to have an assessment of the synthesis methodology and its scalability.
- The project’s relevance is sustained by the fact that the ANL team is investigating how the ink solutions are affecting the dealloyed catalyst and providing characterization. If the project was just an MEA integration project, there would be some question as to whether this effort was simply relevant to the catalyst being used, or to the processing methods that have been selected. However, the researchers have instead directed the project to a basic level. Decline in high current density performance (and beginning-of-life low performance at high current density) has been a problem for Pt alloy oxygen reduction catalysts. Studies of proton conductivity in the catalyst layer are highly relevant so long as state-of-the-art materials are being used or there is some way to translate the findings to the use of state-of-the-art materials.

- This project has the potential to advance progress toward DOE goals and objectives, if the relationship between the structure of the catalyst layer and mass-transport overpotential will be established.
- This project is looking for only a very limited improvement in cathode catalyst layer performance—just the part of the polarization curve beyond 1.2 A/cm^2 is targeted. Some fundamental issues with the alloy catalyst were identified, such as movement of the Ni in the membrane, which is quite valuable information about the stability of the alloy catalysts.

Question 5: Proposed future work

This project was rated **2.9** for its proposed future work.

- The future work described is aligned with the proposed work of the project.
- Overall, the future work is well planned.
- The project has a well-thought-out approach, and the future work is appropriate. An increased emphasis on in-cell diagnostics to understand losses is required, and this is planned. An area to consider for high current density effects is the effect of water saturation levels with thin catalyst layers.
- The four major categories of what the project proposes to do could be very simply broken down as the following: (1) studying where dealloyed Ni goes throughout processing, (2) processing parameters versus performance, (3) structural characterization and mapping, and (4) collection of layer transport and kinetic properties. All four categories of elements to study in a catalyst layer appear to be covered: processing, properties, structure, and performance. It is not clear whether, and how, all of these elements of the study will be coordinated with each other. It may be interesting to include some awareness of durability as all the other parts of the study come together. The development of catalyst cracks should also be kept in mind because processing parameters are varied.
- Further work should be done to understand the stability of the alloy catalysts; if Ni does move in the MEA, then this could be a show stopper for this type of alloy. The impact of this Ni movement should be investigated prior to doing more optimization of the catalyst layers.
- Because local O_2 transport resistance is responsible for the high voltage loss at high current densities, future work should include identifying and quantifying the local resistance and developing a method to mitigate it.
- The future work focuses on finding ways to improve interactions between the ionomer and the catalyst surface; the exact path for doing this is not very clear. The role of functionalized carbon is not clear. The effect of Ni leaching will be addressed through the addition of Ni^{2+} into electrode layers, but strategies to mitigate Ni leaching should also be considered. Strategies for addressing mass transport losses are also not very clear.
- The objective of the Monte Carlo model is unclear. This was not discussed at all! Based on the information given, this model serves no useful purpose and likely duplicates activities of project FC-049. It would be much more useful to measure the ionomer layer thickness and stability of the functionalized carbon support than performing impedance measurements to separate mass transport contributions and characteristics of the functionalized carbon. It is unclear how the mass transfer contributions can be separated because only a single loop is generally observed at low frequencies (Nyquist plot). The functionalized carbon characteristics are not useful if the treatment is not stable.
- The motivations for the next steps of this project are unclear:
    - It is not clear how adding Ni ions to the ink will help. Presumably, one would have to add a salt, such as nickel sulfate, but then sulfate ions will also be affecting things. In addition, it is unclear why any of the leached Ni would remain during electrode fabrication.
    - The next three tasks seem predicated on the notion that high current limits are due to poor ionomer/catalyst contact. Working on optimizing the inks is useful, but there are no tasks that will address possibilities for low high-current performance.

Project strengths:

- Organizations involved in the collaboration include those that are very strong in their fuel cell depth (e.g., ANL, GM, and JMFC). ANL seeks to take advantage of recent good work in other projects developing alloy catalysts. ANL seeks to address major questions that could result in considerable benefits if answered correctly. Those questions include: (1) why an alloy catalyst performs worse at high current density, and

(2) how a catalyst layer structure/properties can be influenced by processing parameters in order to achieve higher performance. ANL has already successfully accomplished the modification of catalyst powder with proton conducting groups, which is impressive.

- The project has a well-thought-out approach with good baseline and catalyst systems selected; a range of solvent and ink properties; and good characterization of the interaction effects of the solvent with catalyst agglomerates, Ni dissolution, modeling, in-cell diagnostics, and concepts for improved performance. The linkage of these approaches should produce strong project results.
- The project has exceeded all of its targets in the first year. The team used an excellent catalyst layer design matrix of a large number of catalysts. Very strong modeling efforts complement the very strong characterization component.
- The team is composed of respectable research organizations with adequate expertise. Overall, the team is equipped with the knowledge base, resources, and industry/academia/national laboratory mix that is required for the success of this project.
- The team has access to sophisticated analytical resources; these should be used more heavily in this project.
- The project has a good team covering advanced catalyst materials and fabrication, catalyst layer characterization, and modeling and diagnostics.
- The project features good team composition and expertise. This project addresses an essential topic for successful fuel cell commercialization.
- The technical expertise and collaborations are strengths of this project.

Project weaknesses:

- ANL will have to deal with hazards inherent in any project where materials are being integrated into layers, including using irrelevant solvents and inking parameters; using irrelevant ink application techniques; and generally focusing on processing parameters that may only be relevant to one particular process, or only on a small scale. The project may not have the right characterization methods for mapping the ionomer, the catalyst, and the pores, so as to understand the structure.
- Modeling must be done in better correspondence with characterization and testing in terms of parameters used. The very important effect of morphology is overlooked. There is no clear strategy for addressing the poor interactions between the ionomer and the catalyst. There is a lack of durability results.
- The project should have started with a well-designed durable catalyst, such as one developed at the end of the GM project. It takes too much effort to develop a working catalyst that is unlikely to be employed in practical fuel cells. ANL should not report modeling results that have been known for a long time, such as “mass transport overpotential not being related to mass activity.”
- The model cannot be evaluated, because details are not given. The model duplicates efforts of another project to create a catalyst layer model. The source of the mass transport loss is sufficiently clear. Additional mitigation strategies would be more beneficial to reduce risks.
- Early in-cell testing was impacted by poor cell compression.
- The project will have a very limited impact with the current target and approach.
- Within the defined scope of work, the project does not seem to have a weakness.

Recommendations for additions/deletions to project scope:

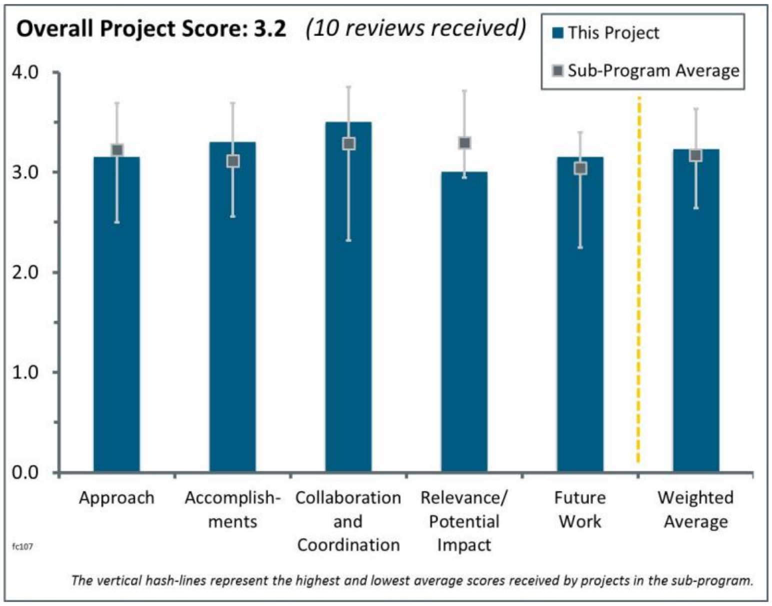
- The project team may want to add other successful catalysts developed under the Hydrogen and Fuel Cells Program, including nanoframe catalysts and mesostructured thin-film catalysts. The team may also wish to add characterization that allows catalyst layer mapping under both dry and wet conditions.
- Porosity/morphology control should be part of addressing mass transport losses. Durability studies must be performed.
- The catalyst with so many problems needs to be replaced by a more stable, highly active catalyst. The optimization of hydrophilic and hydrophobic properties of the catalyst layer should be one of the priorities of this project.
- The project team should change the scope to investigate the stability of the alloy catalysts in operating fuel cells. Good progress was made in this area, and it is very significant if the Ni is moving about the MEA as shown in the data.

- ANL should eliminate planned modeling activities and integrate the work completed in project FC-049. ANL should eliminate efforts to understand the source of the mass transport loss and increase activities to address it.
- It is necessary to conduct a durability study of the rationally designed catalyst layer even if it is not in the scope of work.
- The team should look at water management effects on the thin catalyst layer and include catalyst layer thickness effects in the study.

Project # FC-107: Non-Precious-Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design

Piotr Zelenay; Los Alamos National Laboratory

Brief Summary of Project:



The objective of this project is to advance non-platinum-group-metal (PGM) cathode technology through the development and implementation of novel materials and concepts for cathode catalysts and electrodes with (1) oxygen reduction reaction (ORR) activity viable for practical fuel cell systems; (2) improved durability; (3) high ionic/electronic conductivity within the catalyst layer; (4) adequate O_2 mass transport; and (5) effective removal of the product water.

Question 1: Approach to performing the work

This project was rated **3.2** for its approach.

- Non-PGM catalysts have improved very significantly, and the progress this team has made is very impressive. This is probably a direct result of creative science, proper modeling approaches, and good collaborations.
- This project is off to a very good start. The results demonstrate excellent performance for a non-PGM catalyst. The approach for developing these catalysts is well founded and is leading to excellent results.
- The strategy used in this project is excellent, incorporating synthesis, fundamental understanding, and implementation of knowledge in the real system; very few details need to be added for this project to be outstanding. One missing element is the in situ characterization of catalysts and determination of the possible active sites. The principal investigator (PI) should develop an in situ protocol to really understand activity and stability relationships during the ORR.
- The approach for improving catalytic activity of non-PGM catalysts and developing optimized electrode structures is well planned out. The approach includes significant characterization to improve understanding of active sites and electrode structures, as well as associated modeling approaches of transport properties within the electrode structure. The approach to addressing durability is less defined, and it is unclear whether the approaches listed to mitigate degradation are consistent with degradation mechanisms.
- The project team explained the potential problems and difficulty of this technology but did not show an effective approach to solve them. It is good to be sticking to hydrogen/air cell performance rather than just RDE. The reaction mechanism needs to be investigated to develop effective approaches.
- The project is a synergetic effort of non-PGM ORR catalyst development, active site determination, and electrode design and optimization. Several routes toward the design of materials are currently being evaluated. The selection of precursors and synthetic routes at this stage of the project seems quite random. The rationale behind selecting the precursors, number of heat treatments, temperatures, etc. is unclear. It is also unclear how the information from three-dimensional (3-D) structure and surface probe analysis is/will be fed back to the catalyst synthesis. The membrane electrode assembly (MEA) testing—both in-house and with industrial partners—is of great importance.
- Transition metal inclusion is not preferable. Nano-XRT appears to be very useful for determining pore structure and unravelling the performance implications of the microstructure and nanostructure of the synthesized catalysts. This project is highly relevant to the commercialization of automotive fuel cell technology—a demonstration of useful and durable non-PGM catalysts would significantly impact catalyst cost.

- This project purports to address the key barriers of activity, durability, and power density, but not cost specifically. The plan and approach are well thought out but fundamentally limited by the focus on non-PGM materials as a means to meet the activity and power density needed for automotive applications. LANL appears to have already exceeded some of its activity targets, but with total PGM loadings (on the anode) that are still far too high. The types of durability tests indicated to be done in the future may not be extensive enough to really explore the limits of these catalysts.
- The main weakness here is the complete lack of cost analysis. A large portion of the driving force toward non-PGM MEAs is their supposedly lower cost. The cost of a full system (from feedstock, including processing steps and added hardware/system cost) should be compared to that of an equivalent power system with PGM-containing MEAs. This cost analysis has to be included, especially in the light of the PI's assertion that non-PGM catalysis work has outgrown U.S. Department of Energy (DOE) Basic Energy Sciences (BES) funding. Non-metal catalysts are so poor in activity that the system cost to get the equivalent power output as PGM-containing MEAs could more than offset the cheaper catalyst cost. This technology is nowhere near maturity and should be excluded from the Program and perhaps funded by BES. The use of super-high-loaded anodes (2.0 mg Pt/cm^2) is a concern. The crossover of Pt may skew the results. Transport property research as performed is a plus. Durability needs to be proven.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- LANL shows one of the highly active non-PGM catalysts. There has been an excellent analytical effort to understand the active sites and optimize the electrode.
- The project has shown excellent progress to date, achieving results that exceed milestones.
- Excellent fuel cell activities are demonstrated, exceeding the milestones for two sets of catalysts. Excellent air performance is accomplished as well. The achievement of a metal-free catalyst is of doubtful importance and relevance. Morphological information is of high importance to the optimization of performance, and the effort the team has made toward extracting morphological information deserves praise. It is not clear how this information will be used to affect the catalyst and electrode structure design. The strategies of altering the morphology of electrocatalysts and catalyst layers are unclear. With the project finishing in September 2014, the lack of durability work is disappointing.
- LANL has made excellent progress; however, some of the characterization results are surprising. Slide 7 shows single atom Fe species (see inset), but the elemental maps in slide 16 show significant segregation of the Fe. If the precursor contains molecular Fe species, it is unclear what causes the large-scale agglomeration of the Fe seen in the mesoscale structure.
- The team has made good progress in meeting its volumetric performance targets in a short time. However, the results are clouded by the exceptionally high anode Pt loadings (0.2–2 mg/cm^2) under which the cathode non-PGM catalyst was evaluated. The anode loading for non-PGM cathode MEAs should be as low as required for PGM cathodes if automotive applications are being targeted (e.g., 0.05 mg/cm^2). The exceptionally high 2 mg/cm^2 Pt loading used in many of the tested MEAs can affect the apparent cathode performance in multiple ways, especially at high power densities. In response to a question from a reviewer, it appears the researchers have not explored anode loadings below 0.2 mg/cm^2. In PGM MEAs, going to ultra-low anode loadings can have a deleterious effect on performance. This range of anode loadings from 0.03 to 0.2 mg/cm^2 Pt should be explored for its impact on the non-PGM cathodes for more honest comparison to PGM MEAs. This will be even more important once high-voltage cycling durability testing of these materials is carried out. Such start-stop tests will cause Pt from the anode to migrate to the cathode and give false impressions of the cathode durability.
- The team has achieved significant improvements in performance versus the previous state-of-the-art technology. The team has made good progress toward the September 2014 volumetric activity milestone and demonstrated continuous improvement of the catalyst and layer. Performance gaps versus DOE targets remain.
- The project's accomplishments have been primarily qualitative; because it appears that the researchers do not really understand the mechanism, it is hard to pose the next-step problems. However, the materials

developed so far finally seem at a stage where the performance is high enough that detailed mechanism studies are plausible, and the team should be congratulated for that.
- CM-PANI-Fe-C performs well in air. It is necessary to investigate the interaction of Fe with other materials in the MEA, such as membrane degradation.
- Considering that this is a new project, a good amount of progress has been made, especially in characterizing the synthesized materials. Although the PIs presented some nice TEM images, there is not much value in them—these are nice pictures without substance. The ORR is a surface process and the PI should focus on that—rather than on defending the possible active sites—and try to uncover the still-puzzling role of 3d cations, rather than focusing on bulk imaging. The "graphene approach" is good, and hopefully the utilization of Raman spectroscopy will be a big help in these experiments.
- The current density targets have been achieved, but the crossover of Pt needs to be excluded to affirm that this activity is not due to Pt crossed over from the anode. A combination of much lower anode loadings (an order of magnitude lower) and post-mortem microscopy has to be performed to validate that the measured activity is indeed purely due to the non-PGM cathode. Furthermore, the iR-corrected targets are misleading unless it can be shown that the added thickness of the catalyst layer does not add cell resistance (then iR-correction would artificially make the catalyst appear active). Non-metal catalysts perform poorly; it is doubtful that they will reach the go/no-go target (more than 250 mV off in $E_{1/2}$). This research should be excluded from this project. Good progress has been made on porosity imaging and modeling. New targets should be coming soon, as per the presenter's comments. Hopefully the targets will be aligned with what non-PGM cathodes need to achieve to be competitive with PGM MEAs.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- A strong degree of collaboration is evident between the project partners. The selected university and industry partners are performing highly relevant work to further the understanding of catalyst activity and catalyst layer structure property-performance relationships.
- Good collaboration is demonstrated, with a large number of partners, and the results from a number of partners demonstrate good integration between project members.
- Collaboration is good, and partners are well coordinated with the leading PI.
- The partners seem to work together very well to help make the project successful.
- There is good collaboration with industry partners.
- This project has a broad and large collaborator list, covering issues from catalyst synthesis to fundamental characterization to original equipment manufacturer stack testing. It has good project management potential, with a highly experienced PI. The project is quite new, so it is hard to see the degree of collaboration of all the collaborators.
- This project has a very strong team, ranging from academia to national laboratories to industry. The only thing lacking is a material supplier. To be a successful candidate to replace a Pt-based catalyst, the potential limitations of scaling up, as well as the cost projection, must be studied in the early stages of development.
- An excellent team is working on the project with clearly defined tasks. The synergism is not seen yet in reality.
- Team interactions between modelers, experimentalists, and microscopists are very strong, except with the collaborators at Waterloo, who seem to be working independently on the metal-free catalysts.
- While each partner seems to have his/her own clear project within the project, they supplement each other well.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.0** for its relevance/potential impact.

- The development of highly active and durable non-PGM electrocatalysts has become a focus of the Hydrogen and Fuel Cells Program, with several projects funded by DOE. The progress made in recent

years by the community is exponential, and the current project builds up from the project team's own expertise in this area and has lots of potential for contributing to continued development.
- The development of non-PGM cathode materials is of paramount importance for the successful implementation of fuel cells in transportation. The challenges are huge, but the seed of knowledge already exists.
- The development of non-PGM catalysts is of great potential impact for lowering the costs of fuel cells.
- The project has the potential to significantly further state-of-the-art non-PGM catalysts and close the gap between Pt-based and non-PGM catalysts. Granted, there are still significant performance gains that must occur for the non-PGM catalyst; however, LANL seeks to understand the entirety of the catalyst synthesis and catalyst layer structure. The understanding of the non-PGM catalyst layer structure is still critical to enabling the high-activity catalyst, but significant progress has been made.
- Progress is certainly being made toward DOE goals, but it remains to be seen whether these materials might rival Pt-based cathode catalysts, which also keep getting better.
- The non-PGM catalyst area is generally relevant if the catalyst can achieve comparable performance with a low-Pt-loading catalyst for both high potential and low potential (high current density area).
- Although good progress has been made, it is still unlikely that the technology will be introduced into automotive applications. The project team should consider non-automotive applications and conduct a feasibility study to determine if there may be an earlier path to a commercial application.
- In this reviewer's opinion, non-PGM catalysts are only going to be a success if their activity ensures that the cost of the entire system is lower than PGM-containing fuel cells. At current estimation (based on the plenary session at the DOE Hydrogen and Fuel Cells Program Annual Merit Review), the catalyst cost is <50% of the system, and is likely to drop lower with development of lower PGM-loaded catalysts. Therefore, this reviewer contends that non-PGM catalysts can only be a success if their cost (including processing steps such as high-temperature pyrolysis) is effectively zero *and* their activity is >50% of that of PGM-loaded MEA's.
- The basic premise of the project—the development of non-PGM cathode catalysts that overcome activity, durability, and power density barriers—seems flawed. It is interesting that the PI did not cite cost as one of the barriers that the non-PGM development project addresses. This is actually good, because the total PGM loading targets of <0.125 mg PGM/cm^2 are sufficiently low that replacing the cathode PGM with a non-PGM would have minimal cost impact. Therefore, the remaining potential impact of the project would have to come in its ability to address the activity and durability barriers, compared to a PGM-based system. It is highly unlikely that non-PGM site densities and site ORR turnover rates will ever approach those of metals. The non-PGM focus on hydrocarbon carbon based materials will not eliminate the carbon corrosion issues at the high voltages that start-stop cycling will produce. Therefore, it is difficult to see what the long-term advantages will be, given the higher risk involved.

Question 5: Proposed future work

This project was rated **3.2** for its proposed future work.

- The proposed future work is reasonable. More in situ spectroscopies are needed to understand the limits and the potential of these types of materials.
- The team has identified all the relevant barriers and challenges.
- The proposed future work is reasonable and enhances the approaches in this project.
- The plans are appropriate and well thought out. The exception may be in the area of durability, where insufficient justification is provided on a path forward having a reasonable probability of success.
- In addition to the proposed future work, the following tasks are recommended:
  - Proposed Task A: Have system-level modeling, including a fairly precise balance of plant (BOP) especially designed for the non-PGM catalyst.
  - Proposed Task B: Identify some potential limitations/difficulties to scale-up.
  - Proposed Task C: Start the cost modeling based on the process issues identified by Proposed Task B in manufacturing and additional BOP systems identified by Proposed Task A.
- Metal-free non-PGM catalysts are preferred because of potential issues with component and membrane contamination. It will be interesting to see the results of the molecular probe approach.

- Optimization work may shed light on the attainability of non-PGM MEAs; the modeling work seems on track. Cost analysis needs to be added, as well as durability studies.
- LANL has a large amount of proposed work focusing on mechanism studies and modeling. More effort should be spent in the initial period on experimentally determining the performance and durability gaps in working MEAs that have membrane and anode characteristics acceptable for automotive applications. This will better define the scope of the cathode catalyst limitations and produce a more reliable set of data for the modeling and mechanism studies. For example, LANL should take the best-of-class CM-PANI catalyst at this time and experimentally determine how its performance and durability (under the most severe kind of DOE-defined CV cycling in MEAs) depends on the Pt anode loading over the range of 0.2–0.03 mg/cm^2, membrane thickness from 20 µ to 50 µ, under a range of wet to dry conditions and cold to hot temperatures. This will provide key information for modeling and identify the factors that will need the most work. As the catalyst development proceeds to achieve higher activities, catalysts can be inserted into the defined MEA structure as a new best of class and the array of tests can be repeated.
- With the project in an early stage, the proposed future work perhaps encompasses too many goals. The team has to focus on down-selecting a promising catalyst, optimizing its morphology in catalyst layers, and performing extensive durability studies of electrode structures.
- It is not clear that a technique such as Mössbauer spectroscopy, which yields average information from the entire sample, will be useful to discriminate between the three kinds of Fe species present. It would be difficult to infer the characteristics of each of the species. Furthermore, Mössbauer spectroscopy may not be very useful if atomically dispersed Fe species are responsible.

Project strengths:

- LANL made strong technical improvements over the state of the art. It has also made significant progress in understanding non-PGM catalysts and electrode layer fabrication to enable the use of non-PGM catalysts in hydrogen/air PEM fuel cells. Very-high-activity of the non-PGM catalyst was observed even before catalyst layer optimization.
- The work on electrode structure imaging and linking to modeling for transport properties provides a good approach to better understand opportunities for optimization of the electrode. The characterization of the active sites should support essential mechanistic studies.
- The project heavily relies on the previous PI’s accomplishments, and this project has the potential to provide many answers to a complex electrochemistry on non-PGM catalysts. It is encouraging that the PIs are focusing on a real problem and are trying to combine fundamental knowledge with real applications.
- This project features an excellent team with clear separation of tasks. It also features a great industrial component, very strong characterization efforts, and excellent achievements in activities.
- Strengths of the project are its great breadth of collaborators and the vast experience of the PI and the PI’s institution.
- New PGM-free catalysts with high performance are a great platform to study the ORR in non-PGM contexts, and examination of these materials is being done systematically with a good team.
- The porosity studies are a strength of the project—perhaps providing knowledge transferable to carbon support work. Each partner seems to supplement the others well.
- LANL has established analytical methodology for non-PGM catalysts (materials and performance).
- LANL has excellent in-house expertise to deal with all aspects of catalyst synthesis and testing.

Project weaknesses:

- There is a lack of cost analysis to prove that this technology is competitive to PGM-containing MEAs. If non-PGMs are not financially competitive, then optimization studies are premature and non-PGM research may have to go back to basic research. LANL should reduce the anode loading in the MEA tests by at least an order of magnitude.
- There is no clear path in synthetic routes. Durability must be a priority for candidate electrocatalysts. The purpose of making metal-free catalysts is not clear, unless they are to be used as a reference to study the active site. There is no clear understanding of how morphological 3-D information and other characterization outcomes will be used as input to alter synthetic routes and the choice of precursor.

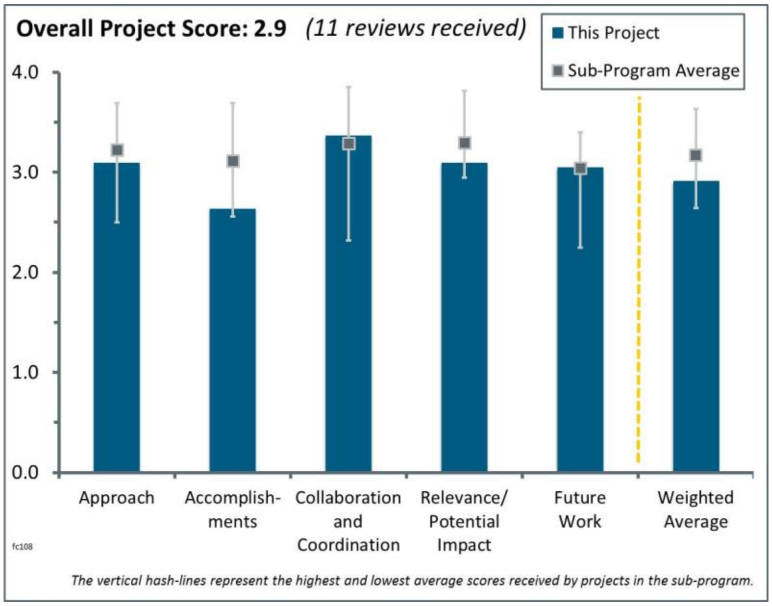
- The explanation of results still heavily relies on a competition of “my explanation versus your explanation.” It is time to demonstrate how stable these materials are and to find a way to quantify the dissolution of active components during the ORR.
- The project’s weakness is trying to optimize the catalyst activity without simultaneously gaining reliable capability for fabrication of electrodes and MEAs that use realistic anodes and membranes, and that only partially test performance and durability.
- Longer-term durability tests are needed to demonstrate the utility of the catalysts being developed. Also, the heterogeneous nature of the catalyst may make it difficult to scale up.
- The metal-free catalyst work seems separate from the other activities, and the performance of these materials is far behind the Fe-containing materials.
- The feasibility for automotive applications is unclear. Durability is a major issue that needs to be addressed. Increased mechanistic studies are required.

Recommendations for additions/deletions to project scope:

- At periodic points, LANL should put a stake in the ground and define a “best-of-class” MEA with the best cathode non-PGM to that point that uses anode loadings and membranes that meet the PGM required targets. The team should do more extensive fuel cell testing with that best-of-class MEA to understand the performance and durability issues that will have to be addressed for competitive performance with PGM MEAs.
- Non-metal ORR catalysts perform too poorly to be funded in an applied research program. The PI should go back to basic research funding (e.g., BES). A full cost analysis (including processing steps, and compared to a PGM-containing stack of equivalent power output) is a must-have.
- From the application side, a purely non-PGM catalyst is not valued. Reducing the use of expensive materials is more important; therefore, opportunities in which these non-PGM catalyst materials can enhance the ORR activity of low-PGM-loading catalysts are of interest.
- If this technology is targeting the automotive application, the competition is the PGM-based catalyst. Without achieving PGM-level activities and high current density performance in air, it will be difficult to use in a product simply because of space issues.
- The team should eliminate the secondary focus on the metal-free catalysts and instead focus on the mechanisms of oxygen reduction in the PANI-based materials.
- The team should pursue better characterization of the active sites in the working catalyst.
- LANL should address anode MEA loadings.

Project # FC-108: Advanced Ionomers and Membrane Electrode Assemblies for Alkaline Membrane Fuel Cells

Bryan Pivovar; National Renewable Energy Laboratory


Overall Project Score: 2.9 *(11 reviews received)*

The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Brief Summary of Project:

The overall objective of this project is to develop advanced perfluoro (PF) anion exchange membranes (AEMs) for improved-performance alkaline membrane fuel cells. Goals include: (1) synthesizing novel PF AEMs with high temperature stability and high water permeability; (2) employing novel PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells; and (3) demonstrating high performance, durability, and tolerance to ambient CO_2.

Question 1: Approach to performing the work

This project was rated **3.1** for its approach.

- This is excellent, groundbreaking work that has a chance to dramatically change the incumbent acid polymer fuel cell industry.
- The project looks to attack the two major problems with AEMs; it is looking at different chemistries to avoid the Hoffman elimination, and increasing water transport. The approaches, in terms of chemistry and fundamentals, are sound.
- The approach for the development of a novel AEM outlined by the project team is focused and addresses the barriers of durability, cost, and performance. The primary focus of the work is on membrane durability.
- The multidirectional approaches taken by the team for the completion of all tasks are adequate. All the analytical techniques had been thought through appropriately. The study on Grignard reagents as a type of “clip on” chemistry amenable to several different well-defined end groups onto PF-sulfonyl fluoride precursor (SFP) side chains is a reasonable strategy.
- This project builds on the principal investigator’s (PI’s) prior and ongoing work, which has U.S. Department of Energy (DOE) Office of Basic Energy Sciences (BES) support, involving new hydroxide-ion conductors. The present project seeks to use knowledge gained from the BES-sponsored work to guide new work making fluoropolymer alkaline ionomer membranes for use in AEM fuel cells (AEMFCs). The project is well designed and addresses the barriers identified by DOE. There are, in fact, only two such barriers in the DOE Fuel Cell Technologies Office’s Multi-Year Research, Development, and Demonstration Plan (MYRDDP), but the project is working toward addressing those barriers and is providing new materials that could help to enable further adoption of alkaline chemistries for fuel cell applications. The approach is well reasoned and sensible.
- The project approach is to address temperature limitations and water permeability with new membranes, which should address the major concerns. The membrane design seeks to separate the electron-withdrawing group from the ammonium group with a benzyl ring, which is good. The perfluorinated design is there for water permeance. The original approach was to use Grignard chemistry, which appears to now be abandoned due to an inability to find a suitable solvent. The project did well to develop sulfonamide linkages in parallel with the higher-risk Grignard route. There is a slight flaw in the approach in that hydroxide conductivity measurements were not yet required within the first year of the project. Instead, the go/no-go decision was allowed to be passed based on IR data on S-F conversion. At this point in the project (especially given that the project is only for two years), hydroxide conductivity data should exist.

- This project is properly focused on facilitating water transport in alkaline membranes. In alkaline fuel cells, the water is produced on the hydrogen side, which does not have a substantial exit flow of inert N_2 to help flush out product water, as there is for the cathode of acid-membrane fuel cells. Because hydrogen recirculation pumps have proven to be difficult to implement, this issue remains quite critical. Claims of alkaline cells being a solution to high noble-metal catalyst costs should be tempered by the fact that the hydrogen evolution reaction is slower on platinum group metals (PGMs) in alkaline than in acid. There is still a catalyst problem; it is just shifted to the anode.
- The project has a sound rationale and scientific approach toward addressing the CO_2 poisoning and water transport issues with alkaline membranes. However, the approach and project timeline should have been much more aggressive to have an impact on reaching the DOE goals for alkaline membranes in just two years.
- The main theme of this project is to use PF polymer as the backbone for AEMs to achieve better transport properties, mainly OH- conductivity and water permeation, and better chemical stability over hydrocarbon-based AEMs. While the PIs are correct that the PF-based electrolyte was proved superior in cation exchange membranes, this does not directly translate into AEMs. In fact, as the PIs pointed out, PF can cause chemical stability issues in AEM due to strong electron-withdrawing PF backbones. It is also debatable whether to expect higher OH- conductivity by using PF backbone in AEMs. Again, the strong electron-withdrawing backbone helps to form stronger acid in proton exchange membranes, but in AEMs, the same PF backbone may cause a weaker base. More direct evidence/data is needed to support the claims of higher conductivity and water transport by using PF backbone in AEMs. Using PF backbone will most likely increase the cost of the AEM itself. Cost/performance benefit analysis is needed at the system level.
- This is almost a basic research project that perhaps should have been funded by BES, except for the drive toward applied goals. The major deficit of the approach is that the membranes are not tested in fuel cells at the National Renewable Energy Laboratory (NREL), and the researchers are relying on a collaborator for all fuel cell performance results. In addition, that collaborator was not responsive as of review time.
- The base for the project is questionable. It is unclear why fluorinated polymer is needed with the hydrocarbon polymer. Amide alkyl has C-H bonds. The whole idea does not make sense.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.6** for its accomplishments and progress.

- The work to date has focused mostly on getting the synthetic chemistry to work well. The researchers have worked hard and had some success, although they also encountered some difficulty. They have demonstrated that coupling to sulfonyl fluoride groups can be achieved, but they do not yet have a good handle on the extent or yield of reactions for the Grignard coupling, the sulfonamide coupling, or the quaternization reactions on sulfonyl fluoride groups in polymers. They have said that future work will include a more quantitative focus on the extent of the reaction; for example, using titration or some other analytical measurement to address how much of the sulfonyl fluoride groups have been converted into sulfoxides/sulfonamides, and ultimately into fixed cationic sites. This focus is good. Studies of conductivity and water uptake may be premature on materials of unknown ion-exchange capacity, so the team should make such studies a high priority in the second year of the project. The team should also start working with hydroxide-exchanged materials as soon as possible. Hydroxide-form membranes have presumably been made, because that is what CellEra will be testing, so the researchers should work on them, too. Studies on chloride/iodide/bromide/PF_6 membranes are fine for a start, but they will not reveal much of what needs to be known to evaluate potential utility in AEMFC technology. Decisions about alkaline stability for ionomer molecular fragments are so far being made just from density functional theory (DFT) calculations; it will be good for the team to start generating experimental results in this area.
- The researchers have successfully demonstrated the Grignard chemistry synthetic route. They have also developed a novel processing scheme to allow Grignard chemistry on PF-SFP. They have successfully used modeling to understand the limitations of Grignard chemistry. They need to find an alternative way to prepare PF-based AEMs.

- Good progress has been made, but many significant challenges remain. Conductivity is still an order of magnitude lower than polymer electrolyte membrane fuel cells (PEMFCs). This looks to be a high-risk project.
- The project team has met its initial goals and shown progress in developing AEMs that can be fabricated into membrane electrode assemblies (MEAs). The conductivities look promising. This reviewer did expect to see OH- conductivities reported at the time of the review.
- Although the idea has flaws, the NREL team made good efforts for the research. The value of the project for commercialization is unclear.
- Two PF AEM chemistries were synthesized. Key characterization data such as OH conductivity and water transport properties has not been obtained, yet the project timeline has passed 50%. It raises a concern about whether the final objectives can be achieved by April 2015. The membrane obtained so far suffers from poor mechanical properties.
- Because this is only a two-year project and the project is 50% complete, it is troubling that the hydroxide ion conductivities of the films have not yet been measured. The MYRDDP has a goal of demonstrating an AEM that retains 99% of original ion exchange capacity for 1,000 hours in hydroxide form at >80°C for the second quarter of fiscal year 2013. The project is far from that goal and has not yet demonstrated hydroxide ion conductivity, let alone durability. Given that it is only a two-year project, the go/no-go decision criteria should have been much more aggressive if progress toward the DOE goals is to be demonstrated.
- So far, the new membrane materials are having numerous difficulties—they are brittle and not yet suitable for hydroxyl ion conductivity testing. There could be issues with water contamination and sulfonyl groups causing crosslinking (and therefore brittleness). The project has less than one year to go and there are still difficulties getting the chemistry to work. It is fair to say that within the next year, it is unlikely that the project will contribute to overcoming the identified barriers. There has been some good work from a polymer synthesis perspective. Materials were made from sulfonamide linkages and some conductivity measurements were made, albeit for halogen anions. DFT modeling has been used to quickly identify alternative synthesis pathways, which has been a highlight. The main issue is the compressed time frame for this project. Investigators are attempting to do about four years' worth of work in two.
- A year into the project, one would expect the researchers to be synthesizing robust films, especially with the competency of the partners. Particularly disappointing is the lack of characterization capabilities at this point in the project. Using other anions as a proxy is OK; however, eventually these characterizations have to be done in the -OH form. The group should have learned how to solve the CO_2 problem by now with commercially available membranes and standardized its testing.
- Membranes have been made in significant quantities, but with only limited testing. More information on the thermal melt process would have been helpful. It seems like that process will affect the performance. DFT seems to be better at explaining observables than giving predictions. Not enough information was given to determine whether the DFT predictions were correct.
- The Grignard-reagent synthetic approach was given a good try and then dropped in favor of using more conventional chemistry to add the innovative spacer sections between the fluorosulfonate and the amine functionality. Conductivity testing of the OH- form of the membrane materials is central to this project and should have been worked out by now—carbonate issues need to be properly dealt with or this project is not doing valuable work.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- The team consists of a good mix of national laboratory and industrial partners. The collaboration with CellEra and 3M is very advantageous to the team.
- The collaborations between the Pivovar group and other institutions are well outlined. Working with CellEra will be of particular benefit because testing the novel membrane in a fuel cell system will best address durability.
- CellEra's insights into the remaining technical problems with alkaline membrane fuel cells have provided an unusually strong level of appropriate focus for this alkaline membrane project that is often lacking in

other such projects. The project appears to be making good use of some of 3M's insights into fluorocarbon membrane chemistry.

- The team is extremely well qualified and the best imaginable to carry out this work. Both a commercial manufacturer and an end user will keep the focus on processability and usability.
- This project features an excellent team that has world-class capabilities in this area.
- This project features good collaboration and a good team.
- Contributions are evident from both NREL and the Colorado School of Mines (CSM). NREL worked on the Grignard route and DFT efforts, while CSM provided other syntheses and conductivity measurements. The project has done well to align itself with both a membrane producer (3M) and an AEM stack original equipment manufacturer (OEM) (CellEra). In the world of AEMs, there are very few players, and this is about as good as it gets. It will be interesting in the future to see more explicitly how 3M is able to contribute toward improving the membrane synthesis routes.
- The collaboration with 3M is important as a source of sulfonyl fluoride polymer materials and should be beneficial in sorting out how to do the reaction chemistry on sulfonyl fluoride polymers. It is not clear what 3M has done so far to help, although this may be due to 3M not being onboard as a partner until relatively recently. The collaboration with CellEra will be very valuable, given its experience with AEM technology.
- The collaborators are clearly experts in their fields and appropriate. Because Los Alamos National Laboratory (LANL) has a long history in this area, which was mentioned in the 2013 presentation for this project, incorporating LANL activities and expertise in the future may speed up progress in materials chemistry and development. It is unclear from the presentation what contributions to materials synthesis and characterization are being made by NREL, and what are being made by CSM. The only clear contribution of NREL is the DFT modeling. The PI should indicate on each slide, where appropriate, the material and information coming from each organization. The roles of the participants in the project are unclear. In the 2013 presentation, CSM's role was listed as AEM MEAs, electrocatalysis, and cell/system testing. However, under the Work Plan, CSM is not listed under MEA testing, but NREL, 3M, and CellEra are.
- The CellEra results are not yet in. No schedule has been given for CellEra to provide results.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.1** for its relevance/potential impact.

- The research being led by the Pivovar group is crucial to the development of AEM technology. AEM technology may surpass polymer electrolyte membrane (PEM) technology in performance and cost, and thus may have a great impact on DOE Hydrogen and Fuel Cells Program goals.
- The project is relevant to the objectives of the MYRDDP. All activities are aligned with DOE's goal. The focus of the project is alkaline membrane development as an enabling aspect of nonprecious catalysis in fuel cells without the concerns of liquid alkaline electrolytes.
- While the future of alkaline membrane fuel cells remains doubtful, this project is focused in determining whether the water transport properties of alkaline membranes can be improved to the point that the disadvantages of water generation on the anode can be tolerated. Office of Energy Efficiency and Renewable Energy funding for this project thus makes some sense, even in light of the significant Advanced Research Projects Agency – Energy (ARPA-E) money that is being expended (with less expert guidance) in this high-risk area. Even if this membrane project meets all its goals, significant additional catalyst work (particularly on the anode) and electrode and cell engineering will need to be carried out before claims of enabling significant reductions of PGM costs in practical fuel cells can be justified.
- There is still a long way to go to demonstrate AEM feasibility. By attacking the key issues with AEMs, this project is of great value to the research community. Successful completion will most certainly guide future research, e.g., on whether perfluorinated backbones should be pursued and what functionalities are suitable for performance and durability.
- Alkaline membrane fuel cell development has been identified in the MYRDDP as an important activity toward reducing the cost of fuel cell systems by enabling the use of non-precious metal electrocatalysts. It may be appropriate at this early stage for DOE, through its Systems Analysis sub-program activities, to

evaluate the feasibility and cost of an alkaline system, because the system considerations are vastly different than for PEMFC, and any materials advantages of alkaline may be negated by system complexity and cost. The project is tackling the relevant issues for developing a feasible alkaline fuel cell, but the progress needs to be accelerated to have an impact on meeting DOE goals.

- This is a high-risk, high-gain project. If this project were to provide a significantly improved AEM that meets the goals of the current MYRDDP, it could enable significant and potentially very important improvements in cost and probably other areas for alkaline fuel cell systems by enabling the use of non-PGM catalysts. It is premature to tell if this end result is likely, but it is surely a goal worth pursuing.
- This is a high-risk game changer approach, so the near-term relevance and potential impact will be low to none on the incumbent PEMFC systems.
- A new AEM is important—it is too early to tell if this is the right approach.
- The project relevance is fairly low because this is a moonshot effort to remove precious metal catalysts from low-temperature, solid-state electrolyte fuel cells. If there were surer routes toward doing this and the development of just one component were the only issue (as is the case for non-PGM O_2 reduction catalysts), the relevance would be higher. As it is, because of the freeze issues entailed in having a stoichiometric feed to the cathode, because of the historic low durability of AEMs, and because of the fairly low power densities associated with AEMFCs, the project has an uphill battle on a variety of fronts. The relevance may still be acceptable for a few LT stationary/portable applications (e.g., backup power, forklifts), but the relevance is low for automotive applications because of the need for water feed on the cathode.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The proposed future work is sensible and well chosen. A focus on the extent of the reaction, including careful measurements of ion exchange capacity, is important at this stage and should have high priority.
- The future work described is aligned with the overall proposed work direction of the project.
- The future plans are well focused and very ambitious. It is unclear whether the remaining synthetic pathway (after the others have been abandoned) has the flexibility needed to realize the project's goal of testing the addition of spaces to improve performance and durability. The intended fuel cell testing will probably require catalyst and cell development in addition to the membrane work described in the presentation.
- The list shown for future work shows that the investigators know what they need to do. Unfortunately, the workload is tremendous for just one year. It would be acceptable to not do fuel cell testing if it means that more time could be spent getting a more durable, higher-conductivity membrane chemistry. Hopefully water permeability measurements will also be included in the future work, especially if time does not permit fuel cell testing.
- The project has an effective approach to the future work. Similar to catalyst development in PEM research, the key feature is the integration of advanced MEAs into short stacks for testing. Durability would best be assessed in the short stack testing.
- In its future work, the team should include characterization of the water transport property, and benchmark mechanical properties against the state-of-the-art AEMs. The chemical stability of PF AEM should be benchmarked against the state-of-the-art AEMs. Cost/performance benefit analysis is also needed.
- The most important focus needs to be generating viable membranes; a support could greatly help the researchers' issues with mechanical properties. Characterization in the -OH form should be addressed in short order.
- The researchers are focusing on improved fabrication, but they are not clear about how the fabrication will be improved. It seems like NREL needs an in-house evaluation effort instead of waiting for CellEra to look at the AEMs and then give feedback.
- The proposed future work is appropriate, but there was little in the way of details on how the future goals would be met, especially in terms of creating dispersions of the ionomers to incorporate into the electrodes.
- Scale-up of any of the chemistries may be a bit premature. The team should do more work on the fundamental materials needed to achieve better conductivity.
- The basic idea has flaws.

Project strengths:

- The project has a good concept that entails separation of electron-withdrawing groups from the anion conductive groups. It also has a good collection of collaborators, including a membrane producer and a company trying to commercialize AEMFCs. Another strength is the use of DFT modeling to direct alternative synthesis pathways. The investigators are experienced with the issues associated with AEMs—these are not people who just heard about this technology last week.
- The team has the experience and will to focus on the critical issues in the development of alkaline membranes for practical fuel cells. A successful down-select of preparative chemistries has been made. This project's plans make more sense than those of other projects in the alkaline membrane area, which is receiving perhaps a bit too much hype in this era of ARPA-E and other programs in which novelty trumps careful reasoning about what realistically can be considered likely to work in practical applications.
- The team is composed of respectable research organizations with adequate expertise. Overall, the team is equipped with the knowledge base, resources, and industry/academia/national laboratory mix that is required for the success of this project.
- The PI proposes a sensible and well-reasoned approach to realizing the substantial cost gains that could be realized if alkaline systems could be used with non-precious-metal catalysts. His approach is based on solid foundational work with fluoropolymer systems and on computer modeling of alkali stability.
- The strength of the team and approach is very good. The approach is fundamental and attacking the right questions.
- The project features a diverse team of experts covering all aspects of chemistry, dispersions, film formation, characterization, MEA fabrication, and testing.
- Strengths of the project are the enthusiasm toward basic research on AEMs and the fundamental reaction chemistry.
- Strengths of this project are its strong team and high-risk approach.
- The approach involves experimentation and modeling guidance.
- The project team is very strong.

Project weaknesses:

- The claim that using PF in AEM can lead to improved conductivity, water transport, and chemical stability needs more direct supporting evidence. The progress is a bit slow; the project could use better planning so that the final objective could be achieved. In the future work, the researchers should include characterization of water transport property, mechanical property, and chemical stability benchmarking against the state-of-the-art AEMs. Cost/performance benefit analysis is also needed.
- "Relevance" statements oversimplify the overall catalytic gains associated with using alkaline-based membrane chemistries. A more detailed description of the need for better water transport in alkaline-membrane systems would have improved the presentation. The project team should not have gotten this far into the project without being able to do reliable conductivity testing of the OH- forms of membranes—halide ions are likely not adequate analogs, at least at higher humidification levels.
- NREL focused on very limited fabrication of AEMs and delving into basic research of polymer synthesis. No progress was made toward evaluating AEMs in an actual fuel cell. The project is not set up so that the researchers can evaluate their products effectively.
- The technical risks associated with the approach are better suited for a project with a four-year duration, not two years. The project has not yet produced hydroxyl anion conductivity data. The chemistries selected have had mechanical difficulties.
- Weaknesses include the results to date, inability to form robust films, and lack of characterization in the alkaline form. Thermal stability (using thermal gravimetric analysis) is of little, if any, value, especially with a different counter-ion.
- Weaknesses include the limited duration of the project and the lack of sufficient funding/activity to accomplish project goals and make an impact on the Program in this challenging area.
- Membrane properties (conductivity) have yet to be assessed in a hydroxide environment. Issues with carbonation can be mitigated with conventional test fixtures.
- The team is having some trouble doing reaction chemistry on polymers—the researchers will have to work hard to overcome these issues.
- The high-risk approach is an area of weakness.

Recommendations for additions/deletions to project scope:

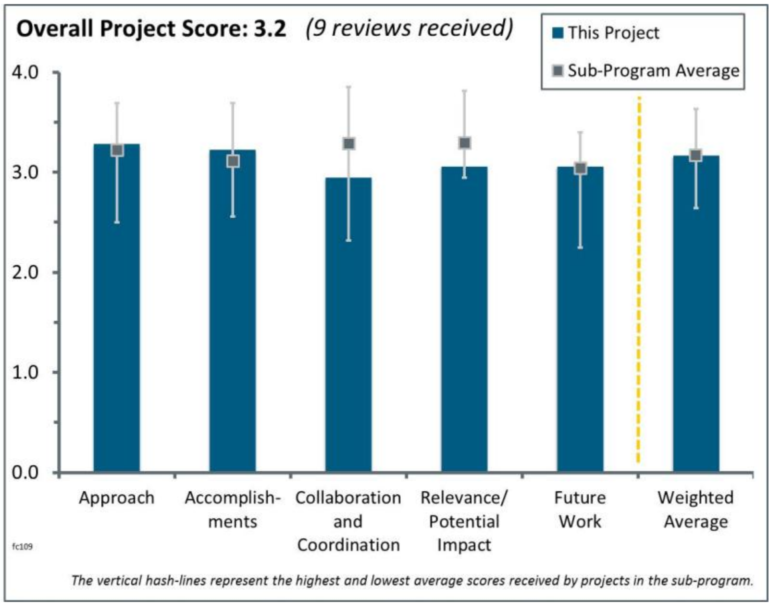
- The PI indicated that in ongoing work he will include a strong focus on the extent/yield of reactions, and on side reactions. This is good.
- There may be some utility in dropping fuel cell measurements from the scope of the project if the chemistry remains challenging. Conductivity, stability (ex situ), and water permeation data can all be prioritized if fuel cell data is not obtained. The water permeability data may be particularly interesting to automotive OEMs that would want to model how an AEMFC would freeze start for a given system operation and cell design.
- In the future work, the researchers should include characterization of the water transport properties, the mechanical properties, and chemical stability benchmarking against the state-of-the-art AEMs. Cost/performance benefit analysis is also needed.
- The researchers should continue to work on the fundamental materials and the synthesis chemistries. Conductivity is still an order of magnitude lower than for acid PEMFC membranes.
- The team should initiate AEM testing in a hydroxide environment. It would be good to understand membranes' tolerance to elevated alkaline exposure pH levels (10–14).
- The project should explain how it plans to address the high-current-density performance of catalyst layers, particularly the anode. It might be wise to include an anode catalyst development aspect in the project.
- The researchers need to get these AEMs tested.

Project # FC-109: New Fuel Cell Membranes with Improved Durability and Performance

Mike Yandrasits; 3M

Brief Summary of Project:

The overall goal of this project is to develop new proton exchange membranes—based on multi-acid side chain (MASC) ionomers and reinforced with electrospun nanofiber structures—that contain additives to enhance chemical stability. The membranes should have improved mechanical properties, low area specific resistance, and excellent chemical stability compared to current state-of-the-art membranes. Membrane electrode assemblies (MEAs) will be evaluated in single fuel cells and fuel cell stacks.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.3** for its approach.

- The approach to develop MASC ionomers, reinforced with electrospun nanofibers and additives, is excellent because it will allow better ionic conductivity at low relative humidity in polymer electrolyte membrane fuel cells (PEMFCs). The side chains are not likely to cause any additional durability issues. Electrospinning is a key skill of Peter Pintauro and may help strengthen the membrane mechanically. It is unclear if electrospinning is scalable.
- The team is pursuing an extension of earlier work, also supported by the U.S. Department of Energy (DOE), on fluorocarbon sulfonimide ionomers, to include ionomers having more than one acid group in each side chain. The strategy seeks to prepare high-conductivity materials that also have good mechanical/dimensional properties, so that all DOE metrics related to membrane properties can be met in a single material. The researchers' approach is well grounded in prior work, quite feasible, and well integrated with other work. They are following a very logical and well-reasoned approach to achieving milestones.
- The project is focused on meeting all the membrane targets simultaneously. The systematic approach to look at varying the type of acid group and number of acid groups on the side chain is commendable. The combination of the support work and the ionomer work should lead to much improved performance and durability. The inclusion of General Motors (GM) for membrane testing ensures that the tests are automotive relevant.
- The project is well laid out and logical. The project is sharply focused on the critical barriers of durability and membrane performance at low RH. One note is that the goals are listed only to 80°C, whereas the Fuel Cell sub-program goals are for up to 120°C operation. Testing was shown at up to 115°C. Although it is stated that cost will be met simultaneously and is being considered, no approach has been provided to meet this.
- The investigators are using incremental changes in chemistry and supports to reach the project goals. They are very close to attaining the goals. Additionally, a thorough look at the sulfonamide functional group, and the effect of having multiple groups on side chains when there is a direct comparison for traditional perfluorosulfonic acids (PFSAs), is very relevant to the community.
- Overall, the approach is good. The development of membranes with new ionomers that have additional functionality for low-RH operation could represent a significant development. Similarly, novel supports could also afford better trades of mechanical properties with resistance. The researchers have a good early

focus on durability testing. The partnership strategy is sound. The approach should include information on the costs of these elements. It is unclear how the costs for both perfluoro imide acid (PFIA) and these various fiber supports compare with unsupported membranes. Cost should be applied as a screening criterion for these approaches to a greater degree than is evident. Although the nanofiber support work may represent an interesting combination, it is not clear why more traditional supporting materials, such as expanded polytetrafluoroethylene (ePTFE), would not be attempted, at least initially. It may be easier to understand the mechanical properties using known versus novel supports. Also, more characterization of the lambda as f(RH) and alpha parameters would be helpful to understand how these ionomers, when embodied in membranes, hold and transmit water. Also, gas crossover measurements should be conducted to inform how the minimum thickness may be affected. Perhaps this was done on the previous award.

- MASCs provide one of the most promising ways to further improve acid fuel cell membranes, which are already good enough for mass-produced applications. These materials were initially developed under a previous project but could benefit from significant additional attention, including the synthesis of further-improved ionomers. It is less clear whether electrospinning will prove to be a useful and practical approach to either membrane reinforcement or casting of the ionomer. A verbal statement that electrospun fibers should not significantly increase costs was not backed up in the presentation by any details that might show that the electrospinning process is manufacturable and cheap.
- This project is working on developing multi-acid chain ionomers for membranes and/or catalyst layers. The project is also developing mechanical support technology (e.g., for composite membranes). The mechanical support materials are based on electrospun nanofibers. The multi-acid incorporation is a side-chain extension from traditional PFSA, incorporating additional SO linkages to improve conductivity. After material development, there is ex situ testing and single cell testing, but limited characterization.
- The project focuses on making membranes and testing their electrical and mechanical properties. The testing of the polymers occurs very late in the project, giving no time to change course if they do not work or break down in the presence of Pt.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- The project is at an early stage, and good progress has been made to evaluate approaches and determine feasibility. The PFIA membrane (unsupported) shows only marginal performance improvement over a 725 equivalent weight (EW) membrane (unsupported). However, the area specific resistance (ASR) shows a clear separation for both supported and unsupported, which provides evidence of a feasible path forward to meeting goals. A number of nanofiber samples have been fabricated on both the laboratory and pilot/production line, with objectives to study various parameters. Good progress has been shown on fabricating the fiber mats, with a number of required parameters identified. There has been good early testing on showing durability; however, it is not clear how much additive is used, and if this is consistent with good performance (e.g., the conductivity tests are likely without the additive, whereas the open circuit voltage [OCV] test is with the additive). Also, a fairly high EW was used for the durability tests, compared to the other testing.
- The work for the present project is just starting to progress, so it is difficult to gauge; however, the researchers have met the milestones they were supposed to have met as of this date and are on track to meet others. A major intellectual advancement for the project is the use of ionomers having more than two acids per side chain. The researchers are not yet reporting on the results from such materials—so far those are just proposed materials. It will be good to hear how well those materials are able to help the researchers meet the membrane milestones all in one material.
- The project has been underway for less than a year. Good progress has been made in screening nanofiber support materials and determining the effect of support on conductivity. The researchers have achieved <5% swell in the down-web direction with 12% fiber content—if this can be met in both directions, the conductivity decrease due to the reinforcement will be greatly diminished. Vanderbilt has achieved electrospinning of PFIA, obtaining identical conductivity for ionomer membrane from electrospun fibers as from solution cast membrane.

- The project has demonstrated considerable progress toward its milestones. The researchers demonstrated that PFIA does not have the EW trade-offs of PFSA and shows potential to hit DOE ASR targets when supported. The supported blend of PFIA and PFSA shows good durability. Results of the durability testing show that the unsupported PFIA meets performance targets but not durability, and vice versa for supported. With the project being so early, it seems that this trade-off will be reconciled. There are questions about the mechanical characterization of the electrospun PFIA. It is unclear how this material serves as a support. If it serves well, it could significantly address the mechanical/conductivity trade-off. Also, the project team should compare supported 3M materials to other commercial supported membranes, such as DuPont XL. Blister strength comparisons to unsupported membranes do not provide useful insights.
- Milestones have been accomplished, showing good progress. Blister strength shows the advantages of the novel membranes as tested using the GM procedures.
- Though it is relatively early in the project, the investigators are very close to the performance targets for the three-year project.
- The project team has made good progress toward scale-up.
- The researchers have demonstrated conductivity of 0.1 S/cm^2 at 80°C and 50% RH; these ionomers are primarily side-chain extensions of more traditional Nafion®. They have made measurements related to meeting the conductivity targets at 80°C 50% RH for PFSA membranes at a thickness of 15.4 microns versus 23 micron thick PFIA membranes, thus showing that they can minimize the thickness of the membrane, which could potentially reduce material costs, but it appears the chemistry is more expensive (8.2 versus 11 micron with reinforcement). The membrane thickness with reinforcement to meet conductivity targets is rather thin; hydrogen crossover numbers should be presented.
    - Made PFIA; measured conductivity and examined water solubility.
    - The nanofiber fabrication by Vanderbilt seems to be progressing well.
    - Looking for a support that provides x-y swelling of <5% after boiling in H_2O.
    - Need 25% fiber content to achieve <5% swelling.
    - Calculating skin layer membrane conductivity separate from the conductivity in the composite layer by making different thicknesses of the skin layer.
    - Completion of RH cycling and OCV testing with PFIA and 825 EW PFSA with a new nanofiber—this shows ~1,500 hours of acceptable performance on the OCV test (with radical scavengers).
    - Blister test conducted at GM.
- Because this project started less than a year ago, it is difficult to give a meaningful grade on its accomplishments. The synthesis of multiple batches of PFIA and the recent preparation of samples with several amide centers on the side chain constitute a good start. It appears from slide 13 that the electrospun materials are still limited to “test patches” of an undisclosed size. To be fully convincing, the electrospun materials will also have to be demonstrated as roll goods. “Welding” times of 10–60 minutes are far too long for a practical process. The reviewer wonders if this could be sped up several orders of magnitude by exposure to vapors at higher temperatures.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.9** for its collaboration and coordination.

- The project features collaborations with GM and Vanderbilt. GM is primarily responsible for ex situ, MEA, and stack testing; it has conducted the blister test to date. Vanderbilt collaboration includes the development of nanospun fibers.
- The collaboration with Vanderbilt is well underway and is already helping the team meet the conductivity and dimensional stability targets simultaneously. The collaboration with GM is longstanding and will presumably become more important as cell testing is undertaken. The direct interaction of this project with other projects is less obvious, but previous projects of a similar nature from 3M have involved many interactions with a variety of partners, so it would be expected that the present project would do the same.
- There is obviously a strong team, with a major manufacturer and an end user. GM screening tools should help the project considerably.
- Good collaborations have been identified. GM is an engaged partner.
- The collaboration with GM shows some usefulness in evaluating mechanical properties.

- There appears to be good collaboration so far between Vanderbilt, 3M, and GM.
- The collaboration should become effective once MEA and stack testing starts at GM.
- In general, it seems that the Vanderbilt support materials have not been integrated to the same degree as the 3M support materials. While this is understandable, more focus should be applied to get the Vanderbilt materials qualified in parallel.
- The role of Vanderbilt is not clear. GM is not participating yet. It is not clear how much preplanning the researchers are doing with GM.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.1** for its relevance/potential impact.

- The project is highly relevant and will have a significant impact. Successful completion would lead to a membrane that allows operation at higher temperature and under drier conditions without sacrificing durability, which would allow reduced systems cost.
- This team is the most likely to meet, or come close to meeting, the fairly aggressive goals originally laid out for the High Temperature Membranes working group. The team has taken to heart the need to meet all milestones simultaneously with one material, and its approach is the most likely to achieve the goal of high conductivity under hot and dry conditions, while still retaining dimensional stability. Achievement of this goal could have a large impact on many goals in the DOE Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan.
- A new, durable, inexpensive membrane is highly desirable.
- The potential impact is significant, particularly if the project can identify ways to solve the performance/durability trade-off, which it seems like it will. However, with no information on cost, it is difficult to understand how scalable and relevant this technology can be at the product scale.
- If successful, the project will significantly impact the ability to operate at low RH, thus supporting reduced cost. However, a critical assumption is that the electrode will not be performance limiting at low RH. There is no mention of work to address the catalyst layer conductivity for MEA integration.
- Acid membrane properties and costs are already good enough for mass production of fuel cells, but improvements would always be welcome. This project has a fair chance of success but would provide, at best, modest improvements in production fuel cell systems. Manufacturability would have to be demonstrated for the electrospun materials. At the very least, a calculation of how many spinnerettes would be needed to produce fibers for a given line rate of X m^2/hour of MEA should be given, and line speeds of mat formation and other post-processing steps should be estimated.
- Currently available membranes meet most of the requirements for PEMFCs and although useful, the development of a novel membrane is not as critical as a novel cathode catalyst.
- The project is just a marginal modification from previous work.
- The work is to achieve more durable low-cost membranes with structural reinforcement.

Question 5: Proposed future work

This project was rated **3.1** for its proposed future work.

- The proposed future work will answer some of the key questions (e.g., the effect of chain extension, how many acid groups is best, and the best method for fiber reinforcement).
- The proposed future work plan is sensible and likely to achieve the project goals.
- The project is well planned out and shows a good path to meeting targets of up to 80°C. However, no path is shown to meeting 120°C operation, and no path is shown on cost. There are alternate pathways on the polymer structure, but the overall approach is relatively narrow. If these structures do not work, there are no additional alternatives.
- The future work is logical and, if it includes the feedback provided, should be able to successfully address the performance/durability trade-offs. The project should explore ways to accelerate materials to larger-scale/stack testing earlier in the project, even if the metrics for those materials are not perfect. Doing this

can help identify and focus scaling constraints that can help focus the down-selection of prime-path materials.
- The proposed future work seems reasonable, although it could be accelerated to be completed in a shorter time by 2015.
- The future work area really needs a contribution in terms of cost modeling for both the PFIA material synthesis and electrospinning of fibers. It is unclear whether these materials will lower the requirements for RH and allow operation at higher temperatures. Measurements along these lines should be made.
- The researchers are about 1/6 through the project and about 90% through the goals; it brings into question whether the funding level was appropriate. Cost analysis would be helpful. It is not clear how the researchers plan to address excess in-plane swelling.
- More attention needs to be paid to the manufacturability of electrospun fibers and their processing into complete MEAs. Testing of newly developed ionomers in more conventional supported and unsupported membranes should be continued.
- The project team is doing a lot of scale up without rigorous MEA analysis.

Project strengths:

- The project features novel concepts for achieving DOE membrane targets. It has a rich design space for ionomer and support materials. The team has made excellent early progress.
- A strength of the project is the path toward a new polymer electrolyte membrane (PEM). 3M is highly competent at membranes and scale-up.
- A strength of this project is its interesting ionomer chemistry. Another strength is its possible ability to tune membrane structure through manipulation of electrospun fibers and the mats made from them.
- The project has an excellent approach; the project lead organization is highly experienced and well positioned to pursue the project's work.
- The project features a strong technical lead and strong collaborators, as well as a clear approach and reasonable probability of success, given the early stage in the project.
- The approach is excellent and addresses three aspects of membranes that could benefit PEMFCs, including conductivity at low RH, mechanical durability, and chemical stability with additives.
- The team members and their expertise are a strength of this project.
- The dual proton conduction site can likely lead to improved performance.

Project weaknesses:

- It is hard to imagine that these PFIA materials are a lower-cost material compared with traditional Nafion, because the chemistry is more complex. The performance may be improved because of the dual proton conducting sites; however, the durability may be less. The researchers should provide some type of cost analysis to evaluate this. It would also be nice to understand the chemical stability of these longer side chains. The electrospun fibers for adding mechanical stability could potentially be a more expensive process than making ePTFE, and the durability may be less because these may be prone to chemical attack. The raw material cost is likely lower.
- Comparison of supported materials to other, commercially available supported materials is an area of weakness. Another area of weakness is the lack of modeling of materials and capital costs to DOE production levels to understand the economic viability of these approaches.
- Testing the new PEMs in fuel cells might come too late to find problems. S and N in polymers might break down over time and poison the Pt catalysts, so durability testing would be key.
- The team paid insufficient attention to manufacturability issues for electrospun materials (at least in the presentation).
- The project is still at an early stage; no results are forthcoming on ionomers with more than one acid in the side chain. It will be good to see results on such materials.
- Cost is not addressed. The early durability testing shown may not be relevant due to the higher EWs used.
- The project may not be scalable, especially the electrospinning.

Recommendations for additions/deletions to project scope:

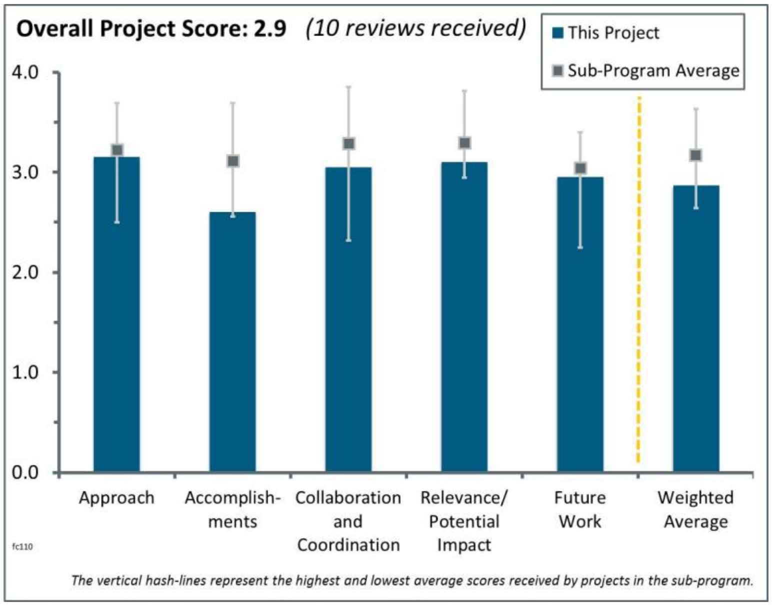
- The project team should make sure that enough testing is done and reported for new ionomers in unsupported membranes or those with conventional supports, as well as for electrospun materials. It should also add robustness (e.g., start-stop, flooded, and dry conditions) to the performance and durability tests planned for the new membranes.
- Both the PFIA and electrospun fibers should be examined in terms of cost and whether there will be a cost improvement. Because the PFIA material is similar to PFSA, there is likely to be an improvement in performance, but not as likely to be an improvement in cost.
- The team should determine the durability of lower-EW membranes—these seem to be necessary for performance.
- The researchers should test the new PEM in MEAs as soon as possible.

Project # FC-110: Advanced Hybrid Membranes for Next-Generation Polymer Electrolyte Membrane Fuel Cell Automotive Applications

Andrew Herring; Colorado School of Mines

Brief Summary of Project:

The overall objective of this project is to demonstrate a low-cost hybrid inorganic/polymer from super-acidic inorganic functionalized monomers with area specific resistance (ASR) less than 0.02 Ω cm^2 at the operating temperature of an automotive fuel cell stack (95º–120ºC) at low inlet relative humidity (RH). The project will also develop a 50 cm^2 membrane electrode assembly (MEA) with desired mechanical properties and durability. The objective in 2014 is to evaluate the ASR for three candidate hybrid inorganic/polymers in practical systems at 80ºC and 45 kPa.



The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.

Question 1: Approach to performing the work

This project was rated **3.2** for its approach.

- The approach to synthesize membranes with tunable proprieties from super-acidic inorganic moieties to produce low-cost, durable membranes seems very solid.
- This project is working on incorporating hybrid inorganic polymers (HPA) into membranes. These materials have the potential advantage of having high proton conductivity at low water content. This project approach is different from other membrane projects and may lead to a large improvement, as opposed to smaller incremental gains. The project is addressing membrane material properties for high conductivity at relatively high temperatures (95ºC to 120ºC) at low RH. Colorado School of Mines (CSM) primarily does material synthesis, followed by partner scale-up and MEA testing. The initial work is related to a previous project nominally on the same topic and is repeating the synthesis work. The project is also working on Pt/HPA functionalized carbons, which is relevant to making MEAs and putting this ionomer into the catalyst layer.
- This project builds on extensive prior work, some sponsored by the U.S. Department of Energy (DOE), on the use of HPA protonic groups in membrane materials for use in polymer electrolyte membrane fuel cell (PEMFC) technology. The approach is fundamentally sound insofar as HPA-based acids have excellent properties, as shown by these researchers in earlier work, and are strong candidates for inclusion in future HT membranes. The Dyneon and perfluorocyclobutyl (PFCB) chemistries both include hydrocarbons that, at least according to conventional wisdom, could be sites for chemical decomposition. Presumably the researchers have a plan to address that, and when they get to the point of having materials suitable for performance testing, this could become an issue. Also, the investigators may not be giving adequate attention to swelling. Many otherwise promising materials have been shelved because they swell too much. DOE targets are pretty aggressive, and in many cases they require that the ionomers are supported in some way (e.g., with a nanofiber matrix). The researchers do not seem to be proposing this. It if fine if they can meet the DOE targets for swelling without supports, but the presentation did not discuss this point much. The researchers should probably address it in future presentations/reports.
- The multidirectional approaches taken by the team for the completion of all tasks are adequate. All the analytical techniques had been thought through appropriately. The study on material synthesis based on functionalized super-acidic inorganic moieties is the reasonable approach.

- The project does address the critical barriers—all of them relate on some level to unit cost, performance, and durability. The approach to solve the problem with HPA and ZrP has been tried in the past with similar additives that have been proven to increase ionic conductivity; however, the basic ionomer was not stable enough (mostly done with sulfonated polyetheretherketone [SPEEK] or some other membrane). This project addresses this problem by using Dyneon, which is a remarkably stable polymer. The only negative part of the approach that has been observed in the past is the washout of these additives as the ionomer degrades, leading to a strong decay in conductivity. The other problem is related to a DOE target—specifically, setting the target in terms of overall resistance. Engineering of the ionomer should be separated from specific material properties. Targets of materials should be set in terms of conductivity or resistivity. Conductance or resistance will be a function of processing parameters to reduce film thickness and area.
- This project builds on the principal investigator’s (PI’s) previous projects developing HPA-containing polymers. His previous work showed materials with promising conductivity at dry conditions that so far have not been repeated with the new project. His approach of relearning what capabilities were lost should enable matching the conductivity of previous materials. His approach to making water-stable, robust, and high-quality thin films is less clear. Only the approach using Dyneon seems to have a path to mechanical stability. While the PI claims to be able to tune the other concepts, the detailed approach was not provided. It was nice to see that the PI is considering cost, but it would be good to see more details about the actual projected cost of the membranes developed, not just the system. A 20% increase from the baseline material set is not acceptable.
- Barriers to be addressed are (A) Durability, (B) Cost, and (C) Performance (ASR <0.02 ohm cm^2, 120°C, 40-80 kPa H_2O). It is very early in the project, and while the high-level plan is laid out, specific details of risks and mitigations are not all clearly addressed. The project is addressing Barrier C first, which is a reasonable approach, as long as sufficient work has been done to confirm a potential path to meeting Barriers A and B, but this is not completely clear. In terms of durability, it was stated that all systems have tunable properties, either co-monomers for desired mechanical properties, or base polymers with desired mechanical properties, and thus the systems should be sufficiently robust. However, it was not clear what the trade-offs would be. To date, at this early stage, there is not consistent robustness (e.g., one polymer is not stable to boiling), but it is stated that this can be tuned to be made stable. The Dyneon-based system was chosen for mechanical properties and is expected to be the most capable of meeting mechanical requirements. The other two systems may have issues. Work to address Barrier B is an initial analysis indicating that costs as low as $40/kW could be attained at high production volumes, conducted using the Brian James model. However, it is not clear exactly how the model is adjusted to get this number, or where the membrane cost estimate is from. Work for Barrier C has been the focus to date and also builds on a previous project that showed very good low-RH conductivity. It appears that the approaches used have the feasibility to meet the performance target, given appropriate processing. However, much work needs to be done. Meeting the ASR is dependent on producing films of sufficient thinness. Two risks seem inherent in this: (1) the ability to produce the thin film with sufficient homogeneity and robustness; and (2) the assumption that the ASR will remain linear with thickness down to very thin films—there may be a risk that surface effects will come into play that result in a non-linearity. In addition, none of the testing has been done at low RH, an essential part of meeting the target. The maximum temperature tested has been 90°C, although the cost modeling was done at 120°C. Overall, it is very early in the project; the technical approaches may be feasible, but there is a lack of clarity on planned approaches to overcome barriers and potentially an understating of the difficulties expected to be encountered.
- It is unclear if it is implied that the fabrication of MEAs will not require the use of a solubilized version of the membrane, because the catalyst layer includes a support that is functionalized with acidic groups. This is an important question because the answer could determine the need to measure the reactant permeability of the polymer system. Questions remain about how stable these acidic groups are covering the catalyst support, what maintains the catalyst layer integrity, and whether any binders are being considered. On slide 6, it is unclear if Year 1 should have been used instead of the Year 2 first-quarter milestone entry.
- The investigators have been at this approach for a long time. It is a given that there is a lack of focus. It is early in the project, but chemistries have not yet been chosen; whether to blend or not to blend, and what type of polymers to blend with has not been thought out or rationalized. There are many promises of good films coming down the pipeline, but they have been at this long enough that many of these issues should have been settled.

- Incorporation of HPA into a membrane could improve the robustness of fuel cell systems by adding another proton conduction mechanism to the membrane. The presentation did not make clear how the present project differs from the earlier project, if at all.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.6** for its accomplishments and progress.

- The team has successfully conducted benefit analysis of a high- temperature electrolyte to show that costs as low as $40/kW could be attained at high production volumes. The team has also demonstrated the challenges and mitigation strategies for film fabrication using HPA-based polymers. The team may think about an encapsulation approach to immobilize HPAs in the polymer matrix.
- Although the project is still very young, the team has already made good progress in producing and evaluating several functionalized polymers, two of which already meet key milestones.
- This version of the project is relatively new, so there are not many new results to report yet. The team is mostly working to repeat prior work and establish continuity with the present project. The researchers obviously have some bugs to work out (e.g., blends comprised of perfluorosulfonic acid [PFSA] ionomers and HPA ionomers have lower conductivity than either component individually, which is obviously not expected or desirable), as the PI noted in his presentation. Conductivities on most materials are not yet very high, and the ones that are high appear to be water soluble. Obviously the researchers have to work out some bugs, but the reviewer is confident that they will do that.
- Because this version of the project has been going for less than a year, it is difficult to generate a meaningful rating for accomplishments. This incarnation of the project appears to have made progress in generating cleaner ionomers than were generated in the past. The project is not as far along at generating testable MEAs as one might have hoped at this stage.
- Even though the project is in the beginning and still gaining traction, some key points are drifting away from the key targets and need reevaluation:
    - The accomplishments with the first two systems are disappointing because the obtained conductivities are not better than state-of-the-art ionomer materials.
    - Ionomer conductivity is being measured at 95% RH, which is different from a typical automotive target of 50%. This is surely due to some limitation in the laboratory, but it needs to be addressed to provide systems engineers with information to calculate cost trade-offs between membranes and humidifiers.
    - There is no need to report overall resistance at this point. The project is about identifying a material that meets specific material targets. Therefore, from now on, the results should be reported as conductivity. Later on, the material can be made to achieve reduced thickness. Also, the researchers should plot a summary graph, with their baseline ionomer and all three systems.
- The purpose of slide 7 is currently unclear in relation to the three proposed polymer systems. It is not clear how this information is going to be used to ensure that one polymer system will meet the <$20/m^2 target. It is unclear if it should be assumed that if the stated cell performance and membrane cost targets are met, then the selected polymer system will meet the system cost target. It is not clear what purpose the co-monomers play during the synthesis of trifluorovinyl ether (TFVE) membranes. It is unclear whether the co-monomers introduce variability in both structure and equivalent weight. It is not clear why it is necessary to add either polyvinylidene fluoride (PVDF) or the 3M ionomer (slide 11). On the summary slide, it is claimed that the films created are robust; however, no evidence was given. Although the three chemistries have the potential to meet the resistance target with thinner films, it is unclear if System III is preferable, considering it will be thicker and may offer more resistance to pinhole formation.
- To date, the accomplishments on this project have been slow; significant work appears to have been required to come up to speed to where the prior project ended. Current membranes fabricated are thick: 107 micron thick film. While this membrane fabrication accomplishment demonstrates the material synthesis, the membranes need to be made with purity, thickness, and quality to be evaluated by the DOE Fuel Cell Technologies Office (FCTO). The researchers needed to relearn multiple synthesis steps—this is why the project should be continuously funded by DOE without gaps. It is also one of the disadvantages of using graduate students, who come and go in projects, because continuous staffing is difficult to maintain and knowledge is not always transferred.

- It is very early in the project (stated 20% completion); the systems chosen have a feasible path to meeting the goals, but there is insufficient information to provide a confidence level on the project's ability to meet the targets.
- There are many comments about work not being performed, or experiments not being reproducible, because the researchers are bringing new students up to speed on synthesis and characterizations.
- So far, the investigators have been focusing on repeating past work. Until they do that, it is hard to evaluate progress.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- The team consists of a good mix of national laboratory and industrial partners. Collaboration with 3M, Nissan, and the National Renewable Energy Laboratory (NREL) is very advantageous to the team.
- Having 3M onboard to supply blending and base materials and to do characterizations is a big benefit to the project.
- The project features good representation of the organizations and expertise.
- The project includes collaboration with 3M in the form of PFSA ionomers that were supplied on an in-kind basis; with Nissan, which will do MEA testing; and with NREL, which is a longtime partner of the PI and his colleagues. Collaboration with NREL and Nissan has not yet ramped up—presumably it will do so as better materials emerge. The degree of interaction with these partners is appropriate at this stage.
- Appropriate partners are identified; however, there does not appear to be much collaboration to date. This is expected to ramp up later in the project.
- The project is relatively new; the contract with Nissan looks like it has not yet been signed. NREL does not yet seem to be involved in this project. 3M is supposed to be involved (in-kind partner); however, its role has not been defined. Also, the project indicated that General Motors (GM) will test materials; however, it has not yet provided materials to GM.
- The "reviewers-only" slide provides a good overview of how NREL and Nissan are involved in the project (not so much 3M—maybe because it is an in-kind partner). However, during the presentation, it was not clear what part of last year's work, if any, was done by these institutions.
- CSM will be interacting with both national laboratory and industrial partners, although these interactions have not yet begun.
- CSM has competent partners in NREL, Nissan, and 3M. To date—which is admittedly early—the contributions from the partners are not obvious. There were no plans shown regarding collaboration with other existing projects.
- Until MEAs can be made, the contributions of other partners will be limited. Collaboration will likely improve as the project continues.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.1** for its relevance/potential impact.

- The project is relevant to the objectives of the FCTO Multi-Year Research, Development, and Demonstration Plan (MYRDDP). All activities are aligned with DOE's goal. The focus of the project is to demonstrate a low-cost hybrid inorganic/polymer from super-acidic inorganic functionalized monomers.
- The project supports all of the MYRDDP goals and objectives related to HT membranes and protonic conduction under hot and dry conditions. The swelling/dimensional stability is a little concerning, and the PI should consider this topic more carefully. If he is able to meet the conductivity targets, his work will have the potential to have a large impact if his materials can also meet the dimensional stability targets and be easily incorporated into MEAs. It is too early to tell yet whether this will be so.
- High-performing, durable, low-cost membranes are needed to enable fuel cell electric vehicle commercialization. These materials must be low cost and chemically robust to meet requirements and be highly relevant, and the project should address these areas as well.

- The project does address the key barriers with System III:
    - Performance: The project seems to be able to achieve DOE targets at 95% RH. However, this RH level is not relevant for automotive applications at HT.
    - Unit cost of $\$20/m^2$: It is not clear how cost estimation of this membrane is going to be done, because it is not shown in the future work. The base polymer itself can probably be made at these cost targets, but the process and raw material costs of the additives should also be estimated.
    - Durability: No information was shared regarding this point, because it was not tested yet. An increase is expected in permeation rates, which would jeopardize the chemical durability and overall catalyst durability due to an increased number of start-up/shutdown events.
    - Efficiency: The idea to go the range of 10 microns will likely result in high permeation rates in order to achieve the target resistances. Therefore, the project should also have a constraint regarding permeation rates, because this would affect the total stack efficiency, which is another important DOE target.
- These materials have the potential advantage of having high proton conductivity at low water content. This project is not meant to make incremental improvements, but to develop basically a new membrane with significantly improved material properties in terms of conductivity at HT/low RH.
- The team aims to produce low-cost, durable, tunable films for fuel cell membranes that will meet critical DOE cost targets.
- The project supports the DOE Hydrogen and Fuel Cells Program’s goals and objectives. However, the automotive original equipment manufacturers have reduced the importance of 120°C, dry performance. A membrane truly able to reach 120°C, dry operation with good conductivity will provide advantages, given the ability of the rest of the system to operate under these conditions (e.g., catalyst layer conductivity and seal and membrane lifetime). However, it is not clear if the rest of the system will tolerate these conditions, and how much advantage will be gained through a successful project.
- The project aligns very well with DOE targets. However, the issues are likely linked to the electrode/membrane interface, but this aspect was not discussed, raising some doubt about the usefulness of the proposed membranes. Inks with solubilized ionomers were mentioned as a possibility.
- No clear demonstrations of the benefits of the inorganic additives beyond what can be done with completely organic membranes were apparent in the presentation or the supplementary slides. The cost analysis seems unrealistic in assuming that the benefits of the materials being developed in this project will allow complete removal of the humidification components and controls from the fuel cell system. Catalytic gains associated with operation at 120°C rather than 80°C are likely to be quite small—the true activation energy (at constant practical potential) for oxygen reduction reaction is considerably lower than the oft-quoted, but inappropriate, activation energies at constant overpotential (the reversible O_2 potential also shifts with temperature).
- It is very unlikely that these materials will be utilized in PEMFCs. Even using the investigators’ most optimistic assumptions, these materials would require a membrane of ~10 µin thickness without a support. This is very difficult, especially considering there is no particular reason to believe that their mechanical properties will be better than current materials that require a support. The investigators are adding PFSA to improve mechanicals, but those require a support at these thicknesses; considering these materials will in all likelihood also need a support, the membrane will need to be very thin. This also brings into question whether the investigators will be able to meet the hydrogen permeability targets or the mechanical targets.

Question 5: Proposed future work

This project was rated **3.0** for its proposed future work.

- The future work described is aligned with the proposed overall work scope of the project.
- The team has proposed a good balance of synthesis development, characterization, and scale-up.
- The project is, at this stage, highly focused on future work because it has just started and the team is still working out some synthesis and membrane processing bugs. The investigators’ plan for future work is reasonable, insofar as it is focused on achieving the goals that were originally set out for the project. It is OK for them to be at this stage now, but a year from now they need to be a little further along.

- The project path is well-defined; the work to make the ionomeric materials relevant to incorporation into catalyst layers is important, although it is not really a membrane project. The PI should be given the freedom to do this because it could lead to an important result.
- One hopes that the people newly trained to make the organic/inorganic composites will continue progress in their training to address the concern of student turnover, to allow attention to be shifted to making good MEAs for detailed testing. Plans seem to be appropriate, but detail is lacking in such items as "Electrode optimization and MEA fabrication."
- The future work listed is the optimization and characterization of the various options, but no details were provided on what characterization would be done and how the optimization would be conducted.
- The high-level plan and milestones are appropriate. Increased details on risk mitigation are needed.
- For System III, the need for an increase in water stability should have been explained.
- It was not clear what membrane properties will be measured next, even though there is mention of a full membrane protocol testing. Systems I and II do achieve the target resistance performance at lower thickness; however, the material conductivity is not better than state-of-the-art ionomers. Thin-film processing on Systems I and II are not recommended, because of this.
- The project is off to a slow start, but it could really use some focus at the beginning. The investigators should settle on a single chemistry, see it through, then double back if needed.

Project strengths:

- This project approach is substantially different than other membrane approaches, and the theoretical possibility of successfully producing a high conductive membrane that requires low RH exists. The project is a departure from the approach taken by many of the Office of Energy Efficiency and Renewable Energy (EERE) projects, which show incremental gains; to achieve this gain, the project requires time to make progress, and addressing short-term quarterly milestone could very well take the project in wrong directions.
- The team is composed of respectable research organizations with adequate expertise. Overall, the team is equipped with the knowledge base, resources, and industry/academia/national laboratory mix that is required for the success of this project.
- HPA acids offer unique and attractive properties for PEM materials, and the lead investigator is ideally positioned to pursue research on HPA-based PEMs. He has a significant amount of experience and has assembled a good supporting team.
- The project shows a path to low-cost, low-RH, high-temperature capable membranes. Three paths are included to reduce the risk of failure. There are feasible paths to also meeting durability. Collaborators will provide strong support and ensure the project is commercially relevant.
- The project features varied and experienced team members. Several polymer systems with adaptable parameters will be explored, raising the probability that at least one will satisfy technical targets.
- Strengths of this project include its experience in handling inorganic proton conductors, and relearning experience used in coupling the inorganics to organics and making workable films.
- The team has a strong background in membrane development and has selected strong collaborators.
- This project is building on the promising results from the PI's previous project.
- The team has a capable group of researchers who are well versed in the field.
- A strength of the project is the use of Dyneon as a base polymer.

Project weaknesses:

- This project, to date, is off to a relatively slow start. This version of the project is relatively new, and due to a lapse from the previous project, it has had to spend time repeating some prior work to bring the project up to speed. DOE funding to make these projects continuous, without lapses, is required to prevent this "wasted" effort. This project seems to be far from making materials that are relevant to the Program. It needs to concentrate on either making, or adding a partner that can produce, these membranes. Knowledge transfer from the previous project, from student to student, apparently was weak. The project partners do not appear to have been incorporated into the project yet. These project partners should be utilized (or a new partner added) to help with producing materials in terms of quantity and membrane thickness for evaluation by organizations like GM.

- The range of materials that the team will investigate is a bit diffuse—aryl trifluorovinyl ethers, Dyneon, and zirconium phosphonates. Only two of the three systems have HPA, and their chemistries are very different. The common theme in the research is not always clear. As the researchers work the bugs out of their chemistry, they may wish to down-select, giving up on some chemistries and focusing on those that are working the best.
- The project lacks a detailed plan. The PI claims to have a large toolbox of thin forming techniques, including solvent casting and thermal and pressure treatments to produce thin, robust films that will also meet the performance targets. It would be good to see more specific details of the plan and why the PI believes that his approaches will work. Otherwise, it seems more like a trial and error approach.
- This project’s slow start is an area of weakness. After many years of investigation, these chemistries still have not shown a large advantage compared to PFSAs in low-RH conductivity. Coupled with all of the questions of stability, mechanical durability, and processability, the investigators have a daunting challenge.
- Project weaknesses include the team’s inexperience with producing Dyneon and scaling up the batch size, as well as processing quality, reproducible thin films. Hopefully the team will be successful with both during the upcoming year.
- Even though Dyneon is a stable polymer, it is not the best ionomer in the industry for conductivity. Other polymers without the additives might still be better than this approach.
- Issues related to the membrane/electrode interface should be clarified and activities should be reinforced, considering they are crucial for a successful integration of the membrane to the MEA.
- To date, no thin films with adequate properties have been made to allow demonstration of the approach in fuel cells.
- There is a lack of clarity on detailed plans and risk mitigation.
- More polymer expertise is needed to prepare a polymer HPA composite.

Recommendations for additions/deletions to project scope:

- The investigators should reinforce activities related to the membrane/electrode interface to ensure the probability of a successful integration of the membrane to the MEA. For instance, at least one additional MEA structure should be considered to reduce risks.
- CSM should concentrate on the chemistry, materials synthesis, and advanced characterization. Either partnering relationships or another partner should be explored to “manufacture” the thin membranes (~20 micron) that will be required to make this project successful.
- The only recommendation is that if the zirconium phosphonate polymers continue to be water soluble, the work on them should probably be discontinued.
- The focus should be more than on reduced thickness and robust films. The team should continue to focus on conductivity improvements, as extremely thin films (<10 micron films will be required for Systems I and II) are likely to have crossover issues.
- The project team should delete activities for Systems I and II. Conductivities measured are low, even at 95% RH. The team should also investigate potential new systems where material conductivity is promising.
- The team should not make any changes to the scope.