2018 – Fuel Cell R&D
Summary of Annual Merit Review of the Fuel Cell R&D Sub-Program

Summary of Fuel Cell R&D Sub-Program and Reviewer Comments:

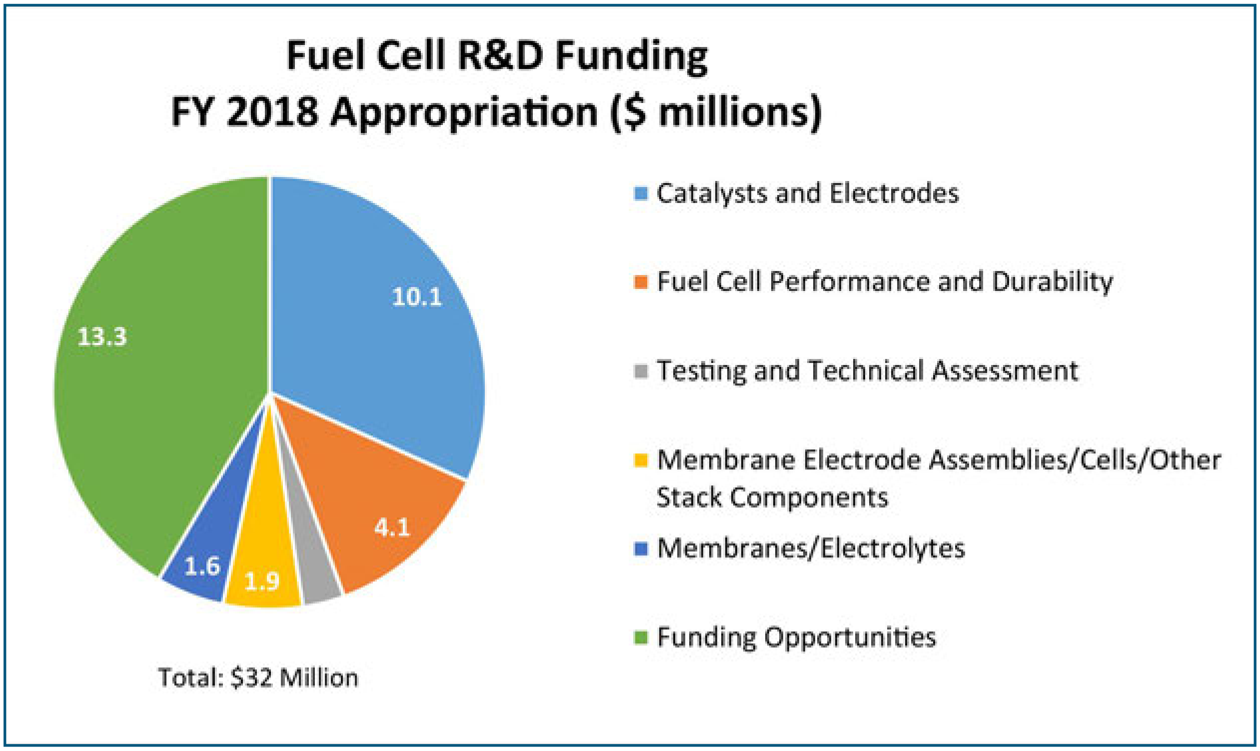
The Fuel Cell R&D sub-program includes a diverse portfolio of fuel cell technologies to enable low-cost, durable, and high-performance fuel cells. Early-stage research and development (R&D) areas in 2018 include catalysts and electrodes, membranes, fuel cell performance and durability, and assessments. Catalyst and electrode R&D comprises efforts on development and utilization of low-platinum-group-metal (low-PGM) and PGM-free catalysts; the latter area focuses on work by the Electrocatalysis Consortium (ElectroCat). Membrane R&D includes polymer electrolyte membranes (PEMs), as well as alkaline membranes. Fuel cell performance and durability is the purview of the Fuel Cell Performance and Durability Consortium (FC-PAD). The Fuel Cell R&D sub-program also includes fuel cell system modeling and analysis, as well as efforts to develop components for unitized reversible fuel cells.

The Hydrogen and Fuel Cells Program (the Program) reviewers noted that the Fuel Cell R&D sub-program has a comprehensive and well-balanced project portfolio. They agreed that the general focus of the various initiatives are in line with the fuel cell industry's long-term needs and address primary issues and opportunities (especially in achieving PEM fuel cell cost reduction with low-PGM catalysts). Program reviewers also specifically noted that the consortia approaches with ElectroCat and FC-PAD are managed well and are the best way to help advance industry and meet future work targets, and should continue to focus on materials properties work in regard to fuel cell catalysts. Reviewers noted that the sub-program needs to do more basic research to make more progress year-over-year in meeting performance goals, especially in terms of the durability technical targets. The sub-program was encouraged to continue to support the approach and collaboration of individual consortium projects. Reviewers stressed the importance of projects focusing on promising concepts such as carbon supports and low-PGM catalysts as crucial components of the pre-commercial R&D portfolio aimed at cost reduction. Reviewers noted some projects, such as reversible fuel cells, represented a low chance of commercialization based on the state of technology. One Program reviewer also noted that projects within the sub-program are relatively small on average compared to similar projects in other countries. Project reviewers were also impressed with specific project-level highlights and accomplishments, as detailed in the project review reports that follow this introductory summary.

Fuel Cell R&D Funding:

The Fuel Cell R&D sub-program received $32 million in fiscal year (FY) 2018. The sub-program focuses on early-stage applied R&D to reduce fuel cell costs and improve performance and durability, as depicted in the figure below. The funding is expected to achieve increased activity and utilization of low-PGM catalysts, PGM-free 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 advanced fuel cell performance and durability. Future work is expected to focus on meeting performance, cost, and durability targets for fuel cells with continued work through the consortium approach, further reducing PGM content in catalysts, and expanding the knowledge base to advance fuel cell performance and durability. R&D will also focus on innovative concepts for reversible fuel cells to provide easily dispatchable power and flexibility to address resilience and grid/microgrid needs.

Twenty-eight projects were reviewed, receiving scores ranging from 2.8 to 3.5, with an average score of 3.16. Each of the following project reports contains a project summary, the project's overall score and average scores for each question, and the project-level reviewer comments.

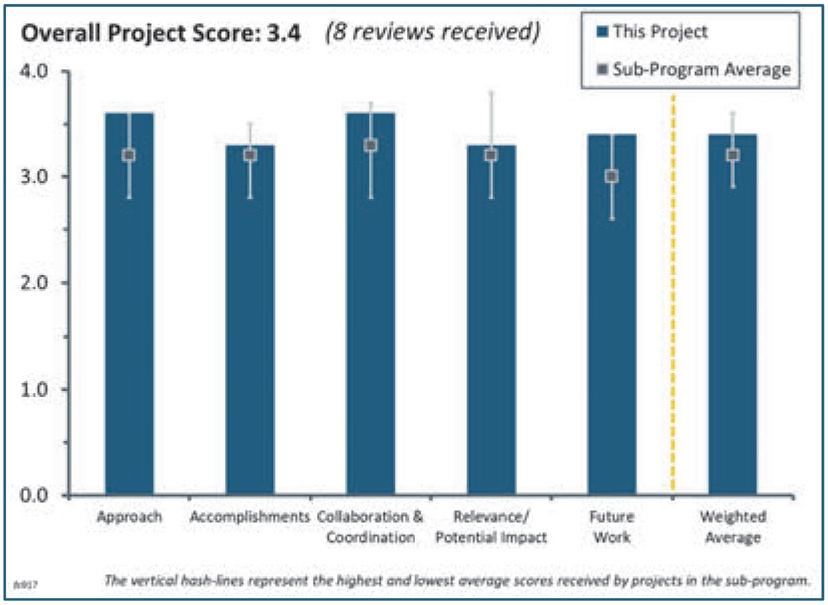

Fuel Cell R&D Funding
FY 2018 Appropriation ($ millions)
10.1
13.3
4.1
1.6
1.9
Total: $32 Million
Catalysts and Electrodes
Fuel Cell Performance and Durability
Testing and Technical Assessment
Membrane Electrode Assemblies/Cells/Other Stack Components
Membranes/Electrolytes
Funding Opportunities

Project #FC-017: Fuel Cell System Modeling and Analysis

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project:

The objective of this project is to develop a validated system model and use it to assess design-point, part-load, and dynamic performance of automotive and stationary fuel cell systems. Argonne National Laboratory (ANL) will support the U.S. Department of Energy (DOE) in (1) setting technical targets and directing component development, (2) establishing metrics for gauging progress of research and development (R&D) projects, and (3) providing data and specifications to DOE projects on high-volume manufacturing cost estimation.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The modeling methodology and procedures are highly developed and thoroughly implemented in this project. The team is also very experienced and responsive to addressing key issues with fuel cell components and materials development. Results have been continually refined to reflect identified issues.
- This work is highly relevant to the DOE technical targets and provides a much-needed stack/system element to help ensure the fundamental materials research is moving in the right direction.
- The approach of the project is technically sound and is providing answers to pertinent questions about the fuel cell system design options available.
- The approach involves development and refinement of a polymer electrolyte membrane fuel cell (PEMFC) system model, as well as use of the model to evaluate design choices. The model is being validated using performance data from ANL and various partners. The approach of investigating various design options and using modeling to predict performance and cost makes sense and is helpful.
- The team uses a well-established design for manufacture and assembly (DFMA) technique, combined with technical input/feedback from multiple project lead investigators, developers, suppliers, and original equipment manufacturers (OEMs) to provide a solid estimate of fuel cell system (FCS) projected costs. In addition, the team pulls on experience performing FCS cost studies extending over roughly a decade.
- ANL developed a validated system model, which allows DOE to guide component targets and project success, and allows Strategic Analysis, Inc. (SA) to estimate the high-volume manufacturing costs.
- The Fuel Cell Technologies Office (FCTO) should have a system-level model to provide inputs into other necessary projects (e.g., cost projections), as well as to inform DOE and others of state-of-the-art (SOA) status.
- The principal investigator (PI) is very knowledgeable in the field, and the approach was well-thought-out.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- In fiscal year (FY) 2018, design choices involving system operating pressure, humidification, and system controls for freeze, start/stop, and idle operation were evaluated. Since much of the existing knowledge in these areas is company proprietary, little is known in the research community, and this project is making a meaningful impact by illuminating these issues and building understanding that will inform R&D decisions.
- Very good progress has been made. It would be good to see more emphasis on incorporating low-electrochemical-surface-area (low-ECSA)/low-roughness-factor catalysts into the model (impact on high-current-density performance).
- Accomplishments are relevant, and the team provides excellent data. It will be interesting to see model validation to give further support to this effort.
- The project showed nice accomplishments this year, in particular regarding the idle state and shut down strategies.
- The PI incorporates SOA materials into the model and provides relevant feedback regarding the impact on FCS operation.
- As usual, many additional good results have been accomplished in the past year.
- The team consistently meets the project goals. As an analysis of the status, it does not directly contribute to advancing the Hydrogen and Fuel Cells Program (the Program) goals, except in terms of assessing progress toward the goals and a modest level of guidance on sensitivities and potential pathways to approach the long-term goals.
- This project has been operational for circa 15 years and has been very helpful in defining issues and progress with detailed fuel cell technology. However, it is not clear whether recent results are being independently validated or incorporated by either other DOE-funded projects or industry. It now appears that current efforts are more or less minor tweaks to existing concepts and systems.

Question 3: Collaboration and coordination

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

- This project has a long history of productive interactions with other organizations concerning fuel cell technology issues. Apparently, the team intends to continue this in the future assessments, including activities with the Fuel Cell Consortium for Performance and Durability (FC-PAD).
- The team is collaborating extensively with multiple partners to guide model development and provide validation data. The collaboration with SA is critical for guiding SA's cost projections.
- This project is engaged with many academic and industrial partners. Overall, there is excellent collaboration.
- The team has consistently had excellent collaboration with various suppliers, developers, project lead investigators, and OEMs. If there were any wish, it might be to have more input from international-based suppliers, OEMs, and organizations.
- This project has considerable collaboration that provides useful and significant data to the project.
- The team has impressive engagement with many OEMs, component suppliers, and others.
- Project collaboration involves industry, universities, and government entities inside the United States and internationally.
- The level of collaboration and coordination appears appropriate for this type of project. Collaboration with FC-PAD and the Electrocatalysis Consortium (ElectroCat) should be enhanced, in particular to integrate durability data from single cells and stacks and performances from new catalysts.

Question 4: Relevance/potential impact

This project was rated **3.3** for its relevance to/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 provides much useful and important information surrounding cell, stack, and system design trades. This work has the potential to increase the speed at which system trades can be performed, saving money for those that leverage the information.
- This project is relevant in that the Program requires an effective tool to assess progress toward Program goals, and also to supply recommendations on how to approach the goals and targets. This project provides this function and consistently meets project goals. The project also is charged with supplying guidance on sensitivities and potential pathways to approach the long-term goals. The team may want to expand opportunities here (i.e., determine what areas should be focused on that will have a marked impact on cost reduction).
- The project is relevant in its role of integrating evolutions of component and sub-component performance as system architectures and subsequent system performance. A valuable impact is helping SA better estimate the cost status. However, the impact might be even higher if the model could have been validated at stack and/or system level and not only at single-cell level.
- Examining system designs and modeling the effects of design decisions on performance and cost are helpful for building understanding and informing R&D decisions. Since OEMs are generally secretive about design decisions, it is helpful to have a DOE project investigating this space.
- This work is absolutely necessary, but because of the nature of the work, is not likely (by itself) to result in a significant advance forward. Rather, it helps to guide future work.
- Modeling is an essential component to research and should be deemed necessary.
- The relevance/potential impact of this project is good. However, it is always limited to looking backwards (i.e., it is unclear what the current SOA is). More sensitivity studies of key variables or components (real or hypothetical) should be done to help identify what improvements could make substantial impacts on cost, performance, or durability. The PI says that he assists SA with making these types of sensitivity assessments, but that is limited to cost only.
- While the project continues analyses that relate to PEMFC performance, including some trades and alternative configurations of balance-of-plant components, it is not obvious that any of these will lead to breakthroughs in meeting the DOE targets.

Question 5: Proposed future work

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

- The future work largely continues the current work in refining system design models and providing input to SA. The project will continue to investigate and evaluate new components, including new catalysts and new electrode designs. The proposed work on plates and flow fields could be helpful because flow field design is a poorly understood subject and most R&D work is performed on suboptimal flow fields.
- Selected topics and plans for remainder of FY 2018 are sound continuations of current efforts. The team is including efforts to address performance of lower-content Pt-based catalysts and platinum-group-metal-free (PGM-free) candidates.
- This is an excellent plan forward. It is suggested that ANL add more focus (some was already present) on the impact of low roughness factor on high-current-density performance. Coupling this with anticipated ECSA loss from cycling, it would be helpful to have guidance for a targeted benzyl alcohol catalyst ECSA. Perhaps including a few possible operating modes/system controls, and describing how that would affect the required catalyst ECSA, could help to guide catalyst researchers/funding toward commercially relevant catalysts (e.g., those that meet the ECSA requirement, as opposed to focusing strictly on mass activity).
- The project's future work list appears sound. It is recommended that ANL perform another round of sensitivity analyses to identify remaining low- or mid-hanging fruit to further reduce cost. Perhaps not all the answers lie in power density. It is also recommended that ANL do a similar analysis to that performed here for PGM-free (and perhaps anion-exchange membrane [AEM]) systems. It might be good to learn

what the status of their FCS costs are, as well as what it would take for them to reach the Program targets (or even to be on par with the conventional low-PGM PEMFC system).

- The proposed future work looks to be more of the same, which is good. However, to be excellent, the PI should strive to generate results that could enable making recommendations on the most important improvements to performance (e.g., system size and weight) and durability.
- The proposed future work is in line with the overall targets. Integration of durability aspects and focus on low-volume manufacturing is appreciated. However, some additional points should be investigated: (1) an analysis sensitivity on stoichiometry ratio (in particular at the cathode), and (2) the use of longer-durability testing data (as 100 hours is very short and 95°C is not representative of real life) coming either from FC-PAD or from ANL tests using current automotive durability testing protocols.
- ANL is taking the input from past reviews to help improve the product output. The approach seems sound and is building upon past results and input.
- Future work is clearly listed and is appropriate.

Project strengths:

- The team has excellent continuity, as the team members have been working in this space and refining their modeling techniques for many years. There have been excellent interactions with partners to provide information about design choices and to provide validation data, which is very helpful.
- The team has an extensive history in FCS cost analysis using a well-established DFMA technique, combined with technical input/feedback from multiple project lead investigators, developers, suppliers, and OEMs.
- The ANL team is highly experienced and skilled in performing the analyses of the PEMFC components and systems.
- The project starts at the cell level and moves into the system level, with design trades at each step. This is a comprehensive model.
- The transparency of system-level performance and cost implications of various materials and design options is a strength, as with the collaboration with FC-PAD.
- This is an important project to support FCTO’s overall mission. The work done is rigorous and substantial.
- This is critical work in helping to guide materials-level research.
- The project has positively contributed toward addressing the technical barriers identified by FCTO.

Project weaknesses:

- ANL should seek to do more sensitivity studies to identify what key improvements can enable substantial improvements in performance and durability.
- The project is mostly dependent on patent literature to learn about design choices used by OEMs. Since OEMs are generally secretive about design choices, this is an unavoidable weakness.
- The model should be validated at a stack and/or system level. It is difficult to rely on a model based solely on experimental single-cell testing results and, moreover, using testing parameters that are severe but not representative of real-life trials.
- The project would benefit from more input from international suppliers, developers, and organizations.
- The project modeling could use more validation and predictive capabilities.
- Increased emphasis on Pt dissolution/impact on ECSA would be beneficial.
- While numerous predictions have been made over the years, it is less clear just how thoroughly these have been vetted by commercial developers and users.

Recommendations for additions/deletions to project scope:

- It is recommended that the project continue at the current FY 2018 level of support.
- Another round of sensitivity analysis to identify remaining low- or mid-hanging fruit to further reduce cost should be added. Perhaps not all the answers lie in power density. Perhaps lower-cost steels should be considered, as well as what would enable their use. A similar analysis to that performed here for PGM-free (and perhaps AEM) systems could also be added. It might be good to learn what their status FCS costs are,

as well as what would it take for these systems to reach the Program targets (or even to be on par with the conventional low-PGM PEMFC system).

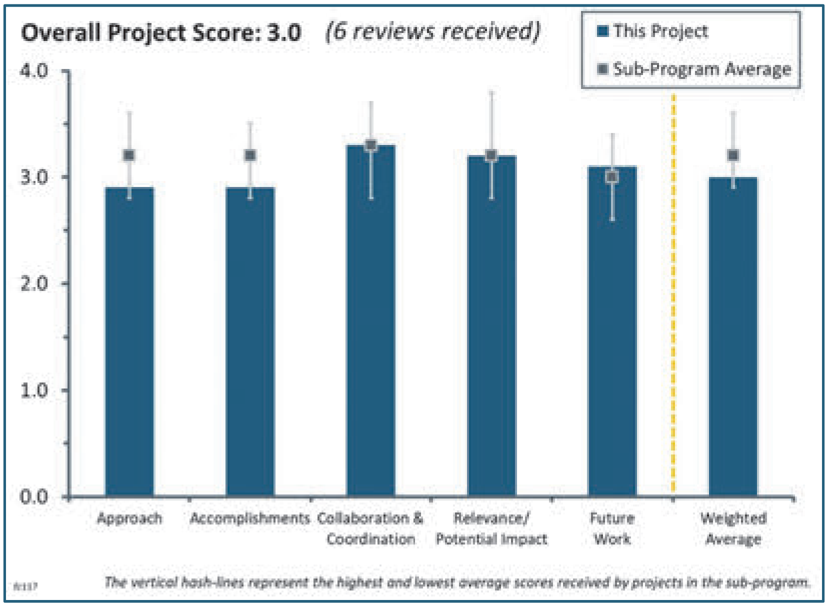
- ANL should investigate the impact of operating modes on Pt dissolution. In general, it seems Pt dissolution is a far more important concern for OEMs than carbon corrosion (air/air events). Understanding this phenomenon and relating it back to catalyst requirements would be extremely beneficial.
- Automotive OEMs should be persuaded to share stack or system data to validate ANL's model under at least a few key operating conditions, with at least one system-level configuration.
- ANL should seek to do more sensitivity studies to identify what key improvements can enable substantial improvements in performance and durability.
- A more mechanistic approach could better direct research.
- Model validation is part of the proposed future plan.

Project #FC-117: Fiscal Year 2015 Small Business Innovation Research (Phase II Release 2): Ionomer Dispersion Impact on Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Durability

Hui Xu; Giner, Inc.

Brief Summary of Project:

To improve polymer electrolyte membrane (PEM) fuel cell and electrolyzer performance and durability, this project seeks to understand how ionomer dispersion affects electrode structures and PEM fuel cells. Specific project tasks include (1) investigation of ionomer dispersion in a variety of solvents and how those solvents affect ionomer morphology and conformation; (2) analysis of how ionomer dispersion affects the electrode function and structure, including ionomer distribution, catalyst distribution, porosity, and thickness; and (3) evaluation of how ionomer dispersion influences fuel cell electrode performance and durability.



Question 1: Approach to performing the work

This project was rated **2.9** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The approach is very good, since it includes a good variety of materials and includes both performance and durability assessments.
- The approach is well-thought-out and contributes to the understanding of the electrode structure and deposition on performance. However, the work presented is narrow, as there needs to be a comprehensive evaluation of more than just physical morphological characteristics of electrodes/membrane electrode assemblies (MEAs) on performance as a result of the solvent used for deposition purposes. What is required are the chemistry fundamentals and influence of the solvent at the molecular level on all the elements of the MEA and the electrode itself. Furthermore, once cells are operated, the system becomes 100% aqueous-based, so an important question is how the different solvents used for the deposition process change or affect performance once the entire system is hydrated, because these are water-based processes. Studies need to include the solvent's effect on the carbon supports, the ionomer particles themselves, and the impact on the interfacial region and membrane after rehydration.
- This project has good relevance, as solvent–ionomer interactions are of interest to the industry. However, there are some issues with the project and/or poster:
    - There is no significant electrolyzer work presented.
    - It is surprising there is no water solvent as a comparison or baseline.
    - Some of the data shown are not clear (end-of-test electrodes seem thicker).
    - U.S. Department of Energy high-level targets are presented, but not this project's specific targets or go/no-go decisions.

  Finally, more work could have been done with the project over three years, such as an ionomer-to-carbon (IC) ratio evaluation for select solvents and their impacts on durability. More electrolyzer work (if that is part of this effort) is necessary. The team should take the best solvent system and optimize it for peak performance and durability.

- In general, the approach was to optimize PEM fuel cells and electrolyzer performance and durability in two ways:
    - By adding ionomers to the electrocatalyst layer to optimize three phase contacts (specifically, the ion conductor, electron conductor, and feed gas).
    - By using different liquid "solvents" that evaporate at different temperatures to dictate the physical phase of the polymer N-methyl pyrollidone (NMP, boiling point 202ºC). Typically, a high-boiling solvent brings the polymer (here it is Nafion) over 140ºC, where Nafion undergoes a phase transition from being a fragile and brittle film to a plastic and tough film.

  It is not clear in this presentation how the project addresses additional technical target tasks, such as MEA mechanical strength and durability, as listed in bullets on slide 2.
- The approach is clear and does improve overall understanding of current catalyst layer design parameters. While this work may help to improve durability, gains are likely to be limited (i.e., no fundamental advance is expected).
- The major flaw in the approach is that the ink formulations and drying methods were not optimized for each solvent, bringing into question the universality of the conclusions. A much better approach would have been to conduct a design of experiments where solvent type was one of the factors. The IC ratio was constant for all solvents. The contents of the solids were not disclosed. Also, while some valuable analysis was done on the inks (although more rheological analyses is suggested) and the catalyst layers before and after durability testing, the correlations between fuel cell performance and ink properties are completely speculative, with no mathematical or mechanistic explanation of the results. There was no attempt to answer the question of why the higher boiling solvents supposedly lead to slower particle growth. Measurements of electrochemically active surface area and activity before and after testing were not disclosed, nor was there any attempt to measure gas transport losses. A more fundamental link between the analysis and the results is required.

Question 2: Accomplishments and progress

This project was rated **2.9** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team effectively met the targets by examining different dispersant solutions of Nafion polymer to alter active layers which have dispersed ionomers, stable electrodes with ionomers, in a processable and scalable way, where most of this is accounted for in terms of the phase transition, which occurs at high-temperature curing of polymers to induce formation of a plastic, tough polymer film in the electrode.
- The lack of optimization work for each solvent system really limits the overall accomplishment of the project. That said, developing a methodology to determine a desirable ink design to achieve optimal performance and durability is a valuable undertaking. However, without coming up with a clear set of design rules, the project results are not universally applicable and can potentially be misleading. A partial set of observations was reported, but there was no clear transferable learning. The authors did well to highlight the downsides of the "preferred" solvents, especially the long drying and mixing times, which make them unattractive low-cost solutions. The most valuable result was the result showing that a relatively small amount of ethylene glycol might be beneficial, thus teaching that investigation of mixed solvent systems may prove fruitful.
- The reported results are quite insightful and valuable, as they shed light on the electrode structure after deposition and the impact of the structure on initial performance. The work on particle size distribution and related data is a good example of progress made in this effort and represents a good starting point. It is not clear, however, how bullet 2 on slide 2 (the Technical Targets) is addressed in this work—a mechanical and chemically stable MEA. The progress reported is focused on ionomer–solvent depositions. Studies need to be performed at a much more detailed level. For example, Nafion-based membranes are exhibiting a much longer life than 5000 hours in non-stationary applications, and have for years. Furthermore, the knowledge and methods for deposition have been developed and used by major commercial suppliers of MEA—hence, it is unclear what is actually new here. The impact after operation for long periods of time in an aqueous environment on the various electrode layers is also uncertain.

- DOE targets are listed, but this project's goals are not listed. Therefore, it is unclear how the project progressed. Good data have been generated, but perhaps analysis has not been done to link the data. The identification of solvent trends could have been pursued more.
- Good progress has been made so far in terms of testing, but so far, the solvent systems have all had a tradeoff in terms of performance or durability; unfortunately, neither can be sacrificed.
- The results are not clearly summarized. For example, the summary states that "ionomer dispersions influence performance." However, the presented results do not indicate that, and when the principal investigator (PI) was asked about it, he stated that there was no performance impact. There is a reported durability impact, but there is no attempt made to summarize this impact in an insightful way. For example, the summary states that "high boiling point solvents greatly improve durability," but this conclusion is not clearly supported. This could readily be done by making a plot of decay (i.e., voltage changes shown in slide 10) vs. solvent boiling point, to demonstrate that this key conclusion is actually supported by the data. Some skepticism of all of the unsubstantiated statements made in the summary seems appropriate, since the statements are not clearly supported and the performance statement is obviously false.

Question 3: Collaboration and coordination

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

- The team collaborating on this project is quite appropriate. All members bring a wealth of experience in not only knowing how to assess the technical parameters of the electrode, but also the knowledge of electrodes in general, in this field. The Oak Ridge National Laboratory (ORNL) team is essential, considering the technical objectives and the focus on the electrode structure and properties; Los Alamos National Laboratory (LANL) and the University of Connecticut (UConn) bring electrochemical know-how and experience.
- Clear contributions were made by all partners. The background experiments for this study were done at LANL, and LANL consultation continued on this project. ORNL's and UConn's main contributions both appear to be in the area of transmission electron microscopy (TEM)/energy dispersive X-ray spectroscopy (EDS) analysis.
- The team partners are complementary and performed their roles well. The dimensionally stable membrane (DSM) was from Giner, Inc., while the ionomer solutions came from LANL. ORNL and UConn contributed to the imaging.
- There is good work by national laboratories on the imaging, which is valuable to this project.
- There are partners, but it is not at all clear what they have contributed to the project—other than UConn, whose activities are actually stated on the acknowledgements slide (TEM/scanning transmission electron microscopy-energy dispersive X-ray spectroscopy [STEM-EDS]). On this slide, the others are simply listed as a "subcontractor" or a "collaborator." What each has contributed should be noted here, at a minimum.
- All project partners appear to be engaged, but it is rather unclear what differentiates UConn's and ORNL's contribution. What capabilities are unique to each institution is unclear.

Question 4: Relevance/potential impact

This project was rated **3.2** for its relevance to/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.

- The potential impact is huge. A long-life, reliable, chemically and physically stable MEA is still elusive with reference to durability and cost, depending on the application. The electrode composition and interactions, if better understood, could lead to long-life, low-cost MEAs, as needed for commercial success. A comprehensive understanding of the elements of the electrode and their impact is ongoing—the work by Myers at Argonne National Laboratory and now More at ORNL are good examples.
- The team performed a needed, important, and non-obvious task for making good MEAs when using Nafion membranes. The results can guide similar developments in non-Nafion polymers. The team should publish these results so others are aware of this, in order to help the technical community develop fuel cells and

electrolyzers. The most valuable contribution here is knowledge about “non-obvious processing” steps for making good MEAs.
- This work is relevant.
- This work is important, and useful information will be (and already has been) generated. However, it appears more incremental (as opposed to a true breakthrough) and of interest to current MEA designs. Thus, it is unlikely to greatly help in significantly closing the gaps on any DOE technical targets.
- Performance and durability are obviously very important, but the impact of this work is not clear for multiple reasons:
    - It is not clear what new conclusions have resulted (relative to previous work in this area).
    - The results obtained here are not clearly communicated (i.e., no trends are clearly reported and substantiated).
    - The impact on performance is negligible, and although there is an impact on durability, this project is not providing elucidation into why.
- Ionomer dispersion impact on fuel cell performance and durability is extremely dependent on the selected ionomer and catalyst materials. A project that focuses on a single material set and does not conduct any optimization studies is not very relevant to those looking for guidance on how to design a high-performing, robust MEA. At the very least, such a project should provide design rules of methodologies that MEA developers could apply. In reality, any MEA developer will conduct its own design optimization studies, and this project really does not teach much that can be applied to help with such optimization. Also, the Pt loading used in this project is too high to be of interest for automotive fuel cell applications.

Question 5: Proposed future work

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

- The proposed future work is reasonable and involves performing TEM of fresh MEAs, compared to decals and decayed MEAs; further testing of the non-aqueous ionomer-based electrode under more realistic accelerated stress testing conditions; exploring state-of-the-art components integrated with non-aqueous ionomers to make low-Pt and high-power MEAs (work to be done in Phase IIB), including high-performance Pt and its alloys and thin membranes (DSMs); and performing scale-up of electrodes (work to be done in Phase IIB). Of the above planned work, there is a need for scale-up and the testing of scale-up as the most important activities. Also, publishing this work in a journal such as *Power Sources* is needed, as a location where developers will learn that this processing is an important goal.
- The future work does sound highly relevant and may result in more meaningful gains in terms of performance/durability.
- Even though the project is complete, some future work was shown. The one valuable set of future work activities was exploring Pt alloys. The other items suggested (such as thin membranes or scale-up) do not add value. Consideration of lower Pt loadings (<0.1 mg/cm^2 Pt) is suggested, as is more than just a single test with a different ionomer.
- The proposed work is not detailed enough. A more fundamental understanding of the interactions of the solvent on the ionomer, membrane, application, and performance should be the primary focus of the next phase of research and development. Questions should be asked related to the preparation history of the membrane, the membrane itself, composition and ion exchange capacity, the method of application of the electrode to the membrane, and the interactions of the solvent with the ionomer, catalysts, and sulfonic acid groups. Even with high Pt loadings on the support, it is still the impact of the solvent on the carbon particle that should be addressed from a deposition and electrode layer characterization perspective. Post-mortems as a function of time should be looked at analytically from a chemical interaction perspective—not just by microscopy and by changes in pol curves.
- The plan is good, but if the execution is the same as in Phase I, then the impact will not be significant.
- The project is completed.

Project strengths:

- The project has a good team with much experience. The potential outcome is quite positive, and the project is starting to look at the ionomer deposition process and the impact on the electrode structure. Giner, Inc.

has the experience in product development from the bench to commercialization—this is very beneficial in focusing the effort.
- Giner, Inc. has assembled a competent team, and the results presented are clear and easy to understand. The TEM/EDS analysis of electrodes is good.
- This is a good topic that does have an impact on both performance (not found here, though) and on durability, which has not been sufficiently explained to date.
- The execution of processing is good, as is the characterization of the results.
- The project contains good data. This was a good opportunity with solvents and included good collaboration.
- This is an important area of work with direct relevance to immediate products.

Project weaknesses:

- The focus is too narrow, and the analyses are not detailed enough. This project does not address all the objectives as listed (at least in this presentation). Knowing that a given deposition process yields good performance is critical and valuable; this work is a start but should have included more comprehensive analyses.
- There is a lack of any optimization work or systematic electrode design, as well as a lack of universality of the approach. The Pt loadings in this project are not forward-looking. No design rules were developed.
- There is limited electrolysis work. Better analysis could further the good data taken. More work and progress could have been made.
- The PI does not appear to be interested in analyzing the data in a way that allows one to draw substantiated conclusions.
- It is unclear how large of an advance in either performance or durability will be achieved by this approach.
- The lack of interpretation and dissemination of the results to date is the weakness of this project.

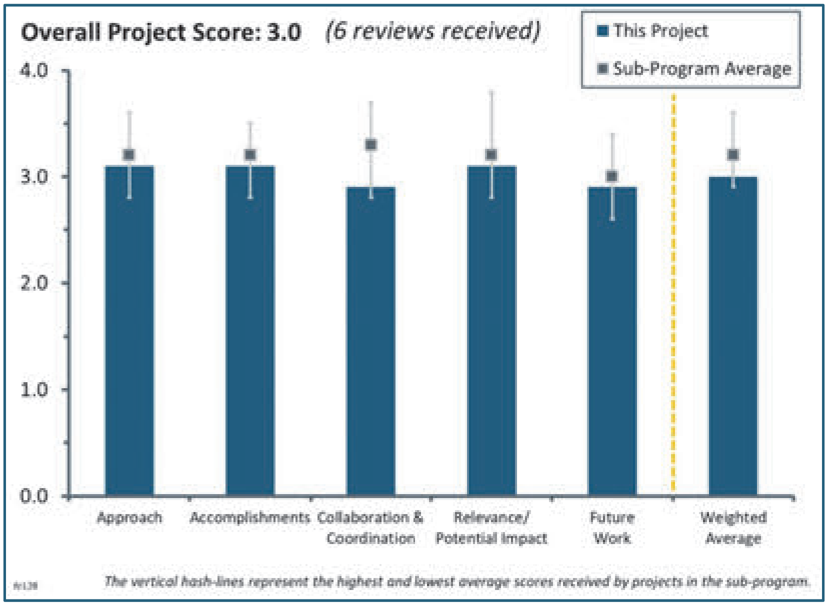
Recommendations for additions/deletions to project scope:

- More comprehensive analytics of the electrode before and after operation is recommended. The cathode is mentioned in this work, but it would be good to know the impact of the anode and cathode in less than 100% relative humidity conditions (as a fuel cell would experience in real-world operations). A broader range of testing conditions is suggested, followed by post-mortems and analyses. Economic estimates of the process based on all the results after the three-year effort should be included if this project receives additional funding.
- More in-depth voltage loss breakdown analysis is warranted on these designs to help with understanding exactly how the different solvent systems are affecting performance/durability.
- It is recommended that the project team do a substantially better job of analyzing the data, such as by making plots to elucidate any hypothesized trends to support key conclusions.
- No deletions are recommended. In terms of additions, developing scale-up and publishing these results are suggested.

Project #FC-128: Facilitated Direct Liquid Fuel Cells with High-Temperature Membrane Electrode Assemblies

Emory DeCastro; Advent Technologies, Inc.

Brief Summary of Project:



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

Dimethyl ether (DME) is a carbon-neutral hydrogen carrier that can be used both for internal combustion and as cost-effective fuel for auxiliary fuel cell power systems in automotive transportation. This project will demonstrate direct DME oxidation with high-temperature membrane electrode assemblies (MEAs) and a Los Alamos National Laboratory (LANL) catalyst. DME is expected to significantly outperform state-of-the-art direct methanol fuel cells (DMFCs). The project will incorporate the new ternary anode catalyst in gas diffusion electrodes designed for high-temperature MEAs, evaluate performance with two different high-temperature membranes (polybenzimidazole [PBI] and tetrapyridine sulfones [TPS]), and optimize structures and reaction conditions.

Question 1: Approach to performing the work

This project was rated **3.1** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- A key metric in this work is Barrier C, related to performance, which is the activity of the high-temperature polymer electrolyte membrane fuel cell (PEMFC) using DME versus methanol (MeOH) as an anode feed and air (or oxygen) as the cathode feed. The team is doing well on this, checking different catalysts and efficiency and power through current-versus-potential (I-V) curves. The challenge for the polysulfone barrier is cost, and Barrier B is associated with catalyst cost; the advantage to cost is simplification (eliminating the reformer), which the team is addressing very well, looking at different materials for anode catalysts and systematically reducing precious metal loading. The durability barrier, Barrier A, is being addressed by the team by examining the temperature stability of two options (PBI and TPS, i.e., pyridine substituted for polysulfone). There could be a good synergy with other workers at LANL looking at the new high-temperature membranes made by Yu Seung Kim et al. Although Advent Technologies, Inc. (Advent) is dedicated to these options, Zelenay is at LANL and may obtain samples for the team. Looking at short-term stability of the DME anode for both the two Advent options and the LANL options seems like a good idea. Another issue is to get some temporal durability data. Although this is application-dependent, it seems wise to screen the membrane by doing conductivity testing (electrochemical impedance spectroscopy [EIS]) over time, testing for a day or so at specific temperatures from the low to the high end of the temperature range. Catalysts should be screened by taking chronoamperograms (current at constant cell potential versus time) under well-defined conditions for at least a day. DMFCs are notorious for high activity for a few hours, followed by rapid decay of anode and anode catalyst in a day or two, followed by very low activity after a week. EIS and chronoamperograms should be done to rate the relative performance of materials and possibly to screen and downselect materials (membranes and catalysts).
- The project approach is innovative: using a fuel cell to oxidize DME at high temperature. However, the advantage, in terms of energy density, of DME compared to hydrogen seems to be outweighed by poor

performance, even at high temperature, relative to PEMFCs. It would be good to know what platinum-group-metal (PGM) loading and performance would have to be achieved to make this more than a niche product for a niche market. Addressing the catalyst and gas diffusion layer (GDL) to improve performance is the right track.

- The project objectives are clearly identified, and the progress to date seems reasonable. However, additional efforts may be needed to characterize the electrochemical performance of the membranes in fuel cells under practical conditions.
- The project is designed effectively to address the barriers such as performance, durability, and cost. This is an incubator project aimed toward DME fuel cells operating at high temperatures. As such, this is a unique project that could not be compared to other similar efforts; however, it is important to mention that the investigators are making significant progress that is in line with previous years of this effort.
- The approach of using a PBI–phosphoric acid membrane is good for using the system under high temperature and thereby harnessing high catalyst activity. However, acid leaching will cause PBI–phosphoric acid membrane conductivity in a direct-water-solution-fed system to change over time, especially under proton flux. This change in membrane conductivity will have an impact on the durability/performance of the system. Under 30 psig backpressure, such leaching will be minimal, but past studies (Plug Power) of PBI–phosphoric acid systems using gaseous hydrogen and air have shown acid leaching/membrane conductivity changes and the need for acid traps to mitigate acid issues. It is not clear that PBI–phosphoric acid is a good separator for such direct-water-fed fuel systems. PBI–phosphoric acid may not be practical for commercialization of a usable system.
- Key barriers have been identified. It is not clear how cost is being addressed, as the PGM loadings for the ternary catalysts are similar to those of the commercial binary catalyst. It is not clear how durability is being addressed (no durability work was highlighted last year or this year), though durability is indicated as a key barrier. The approach appears to focus on optimizing Pt-Ru-Pd, without having clear evidence that Pt-Ru-Pd offers increased activity over commercial Pt-Ru. Analysis of activity on a PGM basis and breakdown of voltage losses appears to be lacking. The project team went through a downselect on membranes earlier but is now suggesting returning to TPS membranes to allow for higher-temperature operation. It appears that some of the requirements were not considered when the downselect was made.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Some very impressive results have been quoted. Meeting and lowering catalyst loading below 5 mg-PGM/cm^2, an order-of-magnitude-lower crossover with DME (6 mA/cm^2) versus methanol (60–120 mA/cm^2), and high short-term power that meets the DOE target of 270 mW/cm^2 were shown at high temperature with the TPS membrane. It is time to begin to screen durability using EIS and chronoamperometry testing, if for no other reason than to rate and to screen materials in a timely way now, before this task is lost, because it may become too difficult to revisit some samples as time goes on. Although it is not necessary, at some point, another possible metric might be to measure relative solubility and/or diffusivity (or the product permeability) of DME and methanol in membranes to see whether this is correlated with the low crossover. This finding might give an easy guide to future development.
- The team has accomplished anode mass activity higher than the DOE target, as well as present anode catalyst mass activity in a DMFC system. The DME crossover target has also been met. DME has lower crossover compared to methanol at 80ºC in a Nafion® membrane because DME has lower solutility in water and also is not a hydrophilic, like methanol. The team did not have much success in reducing the total PGM loading and is not close to the DOE target. Also, the maximum power output is only 50% of the target and lower than the maximum power of a DMFC system. Interestingly, the team used water to evaluate the LANL ternary catalyst, which has the same I-V performance as a binary Pt-Ru catalyst/1.0 M methanol. However, in the present work, the binary Pt-Ru catalyst system worked well with DME fuel, which is contrary to the I-V curve shown in slide 4. The team gave no clear explanation of this behavior. The performance in slide 4 was with direct-fed DME gas, while the team used a DME:water 1:3 solution for the project work. It is not clear why the team decided to change the fuel from DME gas to DME solution.

- Some important progress has been made in synthesis and fabrication of membranes and in characterization of some properties of the membranes under simplified conditions. However, it seems that additional efforts are needed to confirm some key performance indicators, especially under practical conditions for fuel cell operation. The principal investigator's (PI's) company does not have facilities for fuel cell operation/ testing. Thus, closer collaborations with a fuel cell developer (e.g., the national laboratory partner) are vital to accelerate the rate of progress and to validate the technical feasibility of the proposed new high-temperature membranes.
- The project has demonstrated gains in performance and reduced fuel crossover compared to a DMFC. Performance gains have been realized in the past year by increasing operating temperature. However, performance is still far short of targets, with power density less than half of target value. The work to date has not shown a clear benefit of the ternary catalyst composition, and data were not presented in a manner to help separate out activity from transport losses to help evaluate whether the ternary has higher activity than the binary catalyst. There has been little progress since last year in demonstrating the ternary catalyst.
- The project is making progress, as evidenced by met milestones and go/no-go's. However, a lack of targets for alternative fuels for fuel cells means that the project can meet self-set targets with high catalyst loadings. PGM loadings should be more reflective of current PEMFC PGM loadings; otherwise, the cost of these devices does not make them appealing.
- This is the last year of this project, and the investigators made significant progress in demonstrating that DME can be effectively employed at high temperatures. The metrics that have been obtained can justify a strong case for further exploration of the DME concept. The project team was focusing on multi-metallic catalysts and insisted on Pd utilization, although there is no clear benefit to Pd inclusion.

Question 3: Collaboration and coordination

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

- The team is excellent and complementary. Advent is taking the lead on the membrane and LANL on the catalyst and testing. It might be good to try other LANL membranes from different researchers at LANL, such as Yu Sung Kim, if this is possible. Exploiting LANL testing on EIS and chronoamperometry to screen durability to complement activity testing may be good to help rate and downselect materials. This would be better done sooner rather than later so as to not lose information, as it may be difficult to "revisit" some materials later.
- The collaborator, Dr. Zelenay's team at LANL, has a wealth of experience in DMFC electrocatalysis and systems. This group is the right collaborator for the project.
- The project has new collaborations with two catalyst suppliers to test ternary catalyst compositions. Collaborations within the project appear to be going okay.
- This is a well-coordinated effort among the participants, with clearly defined roles.
- It appears that some collaboration exists; however, coordination between partners could be significantly improved, especially in the area of critical evaluation of the membrane characteristics and long-term stability under practical fuel cell operating conditions.
- The extent of collaboration is not clear. If LANL is making and testing the catalyst, which is the bulk of the results, as indicated in the slide, it is not clear what Advent is doing.

Question 4: Relevance/potential impact

This project was rated **3.1** for its relevance to/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 work has its greatest use in portable power: auxiliary power units, portable electronics, scooters, etc. These are needed for a broad spectrum of uses, including military and commercial and emergency power. Developing these markets can be profitable and can stimulate developments in larger applications such as automobiles and heavy vehicles.
- Since the development of high-temperature polymer electrolyte membranes (PEMs) is vital to a new generation of fuel cells, the project aligns very well with Hydrogen and Fuel Cells Program (Program) and

DOE research, development, and demonstration (RD&D) objectives. If successful, the project has the potential to advance progress toward DOE RD&D goals and objectives.

- Overall, using direct-fed DME is expected to have great benefits. The projected source-to-use cost is lower than DOE's target. However, DOE's high-temperature direct DME fuel cell targets are very challenging, and significant technical breakthroughs, especially in catalyst and membrane technologies, are needed to meet these targets.
- DME makes sense as an energy carrier and a fuel. It is not clear how projects directed toward direct liquid fuel cells overall and this project in particular fit into the overall Program. The Program is increasing focus on developing a hydrogen infrastructure, and the fuel cell efforts are moving away from PGM materials to PGM-free materials as catalysts. Direct liquid fuel cells promote non-hydrogen fuels and send the message that hydrogen is not an adequate fuel and alternatives are needed. This is not the message to send when trying to increase acceptance of hydrogen as a fuel and trying to increase hydrogen infrastructure. Direct liquid fuel cells, and this project in particular, utilize PGM-based fuel cells with high PGM loadings. The targets for this project will result in a fuel cell that obtains <0.1 W/mg PGM or requires >10 g PGM/kW, approximately two orders of magnitude more Pt/kW than current PEMFCs. This appears to be at odds with the current direction of the Fuel Cell R&D sub-program that is emphasizing PGM-free catalysts and phasing out low-PGM catalyst work. It does not seem logical to carry out work on high-PGM-loading direct liquid fuel cells when low- and ultralow-PGM-loading catalyst work is being curtailed.
- It would be difficult to judge to what extent this project would contribute to progress toward Program goals, since this is an incubator project. As of now, the prospects are on the positive side.
- Alignment with Multi-Year Research, Development, and Demonstration Plan goals is poor. The technology requires DME production from hydrogen, and the performance would have to exceed that of PEMFCs at reduced cost. However, the PGM loading and operating temperature characteristics are not ideal.

Question 5: Proposed future work

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

- The project is doing well in addressing the issues the team has identified, such as establishing designs of experiment for improving both the catalyst and membrane and for developing and improving short-term behavior, and finding marketing partners. It is time to screen temporal durability.
- In the last year of this project, not too much remains to be done, except to scale to 50 cm^2 MEAs and to demonstrate projected power. That seems logical and appropriate.
- The proposed plans are largely built on past progress and appear logical. However, some of the critical indicators of the membranes are yet to be validated under the fuel cell operating conditions. It is suggested that more fuel cell testing be performed to confirm the long-term stability and performance of the membranes under practical operating conditions (e.g., subject to large current flow at high temperatures).
- The proposed work covers the incomplete milestones, 5, 6, and 7. However, the team did not propose milestone 8, which is to prove that the performance of a direct DME fuel cell high-temperature MEA is higher than that of a DMFC (slide 3). The team also did not mention measuring the "degradation rate" and "start–stop mediated performance loss." It seems that the team is running short of funding and cannot conduct these tasks.
- The project has little time left. Plans address the appropriate issues but are short on some specifics (for example, types of additives that increase DME solubility in phosphoric acid) and on how catalyst activity will be improved.
- A bulk of the work, such as scale-up and GDL optimization, is packed into the last few milestones. It is not clear what the pathway to achieving that is or what steps the project will take.

Project strengths:

- The project team is well assembled, and the investigators have demonstrated the proof of concept for effective utilization of DME fuel cells at high temperatures. The approach is well justified by the outcome of this project, and the PI clearly presented the benefits for this type of fuel cell.
- Achieving a fuel cell with an anode operating directly on an organic fuel with no reformer requires innovation. Since DME is like diesel fuel, this is very attractive, since DME is or can be a logistics fuel.

- The team consists of well-qualified investigators and scientists. The team also has access to top-class research facilities for conducting the proposed work.
- The development of high-temperature PEMs is important to the next generation of high-performance fuel cells. The proposed new membranes seem to be interesting, with some good progress being made. However, additional efforts are needed to demonstrate the anticipated benefits of the proposed membranes in actual fuel cells under practical operating conditions.
- The project is unique in that it is a commercial MEA manufacturer looking at direct DME fuel cells.
- The product exceeds MeOH performance.

Project weaknesses:

- There has been a lack of temporal screening to this point. This screening is important, as this DME technology is an alternative to DMFCs, and temporal stability has been the Achilles' heel of DMFCs.
- The overall relevance to the Program focus is low. The catalysts being studied have not demonstrated the expected advantages over commercial catalysts.
- There is no work on stability, PGM loading is very high, and GDL work was left to the last minute.
- The use of a phosphoric-acid-doped PBI membrane for a direct-water-solution-fed fuel system is a weakness. Much past research has demonstrated the instability of such acid-doped polymeric membranes, even under cathode water vapor condensation. Why the team selected such a membrane is unclear.
- Key performance indicators (including long-term stability) have yet to be demonstrated, especially under fuel cell operating conditions.
- Not much weight is placed on durability, which was mentioned as one of the main barriers.

Recommendations for additions/deletions to project scope:

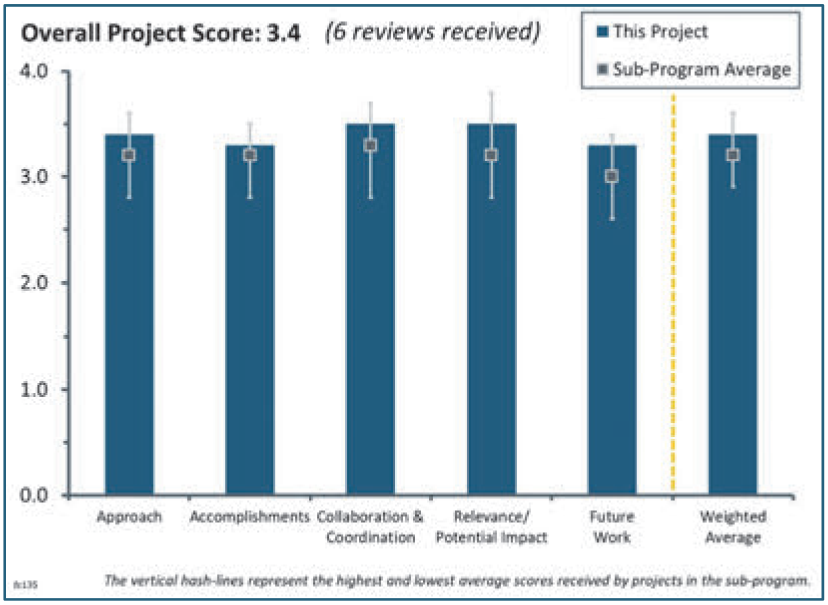
- There are three suggested additions: (1) expand to include other LANL membranes, such as the ones developed by Yu Seung Kim, if LANL and Advent corporate agrees; (2) conduct temporal screening of membrane conductivity at lower and upper temperature limits using EIS; and (3) determine catalyst stability over time at optimal fixed load (cell voltage) using chronoamperometry.
- The project is ending in December 2018. The team does not have much time to work on any proposed addition or deletion in the project. However, if possible, the team should evaluate a direct DME vapor (pressurized 30 psig) -fed system using the ternary catalyst in combination with the acid-doped PBI membrane under high temperature (240°C). The resulting data will help the team determine whether the ternary catalyst (Pt-Ru-Pd) performs better than the binary (Pt-Ru) under high pressure and temperature.
- A drastic loading reduction is needed, on par with PEMFC loading targets. Perhaps accelerated stress testing should be considered.
- Closer collaboration with the national laboratory partner is needed to perform further evaluation of membranes under practical fuel cell conditions.
- Durability should be added in the final report.
- There are no recommendations for additions or deletion to scope. The project is almost complete.

Project #FC-135: Fuel Cell Consortium for Performance and Durability

Rod Borup; Los Alamos National Laboratory

Brief Summary of Project:

The Fuel Cell Consortium for Performance and Durability (FC-PAD) coordinates activities related to the denoted development areas and supports industrial and academic developers. This effort aims to advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs). Researchers will develop the knowledge base and optimize structures for more durable and high-performance PEMFC components; improve high-current-density performance at low Pt loadings; improve component durability; and develop new diagnostics, characterization tools, and models.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The approach of coordinating the investigation of the performance and durability of fuel cells through a consortium composed of the best available experts of national laboratories in a five-year project is excellent. The addition of complementary projects with other industry and academic partners completes this approach in a very efficient way.
- The project addresses critical barriers (catalysts, electrodes, and durability) that currently inhibit fuel cells from commercialization. The provided results regarding catalyst degradation, carbon corrosion, and losses due to deficits in the electrode structure are very insightful and help with understanding how to optimize the electrode structure in order to reduce platinum-group-metal (PGM) usage as well as improve durability.
- The FC-PAD approach appears to be working well. The project team is conducting significant and valuable work. The overall approach is at the correct level: pre-competitive understanding, with thrust areas that are appropriate, well defined, and well aligned.
- This project has a very structured approach, combining the strengths and capabilities of the different national laboratories involved.
- A partnership between national laboratories and other organizations is proposed to diversify the research and bring novel ideas for consideration. Four ideas (projects) have been added since FC-PAD's inception. Additional ideas would be beneficial, considering FC-PAD's scope with five participating national laboratories. The project objectives are to develop a knowledge base to mitigate mass transport losses in the catalyst layer (increased performance and lower cost) and extend lifetime without system mitigation measures. These will be achieved with characterization techniques, testing, and modeling activities. The topics currently focus on cation migration in the membrane, platinum alloy dissolution, and carbon corrosion. Mitigation strategies include ordered array electrodes and other approaches that are not ready to be divulged. The project team does not currently prioritize fuel cell contamination, although it is mentioned. This is rather surprising, considering the cost associated with system redesigns if contamination testing is delayed until an application reaches a higher technology readiness level (TRL). Also, problems are expected with ongoing vehicle deployments, especially because a number of issues are still poorly understood, including the use of cleansers to clean parts, low-catalyst-loaded electrodes and thin

membranes (smaller sulfonate site inventory) exposed to contaminant mixtures, and absence of stack-level recovery procedures.
- The central idea behind FC-PAD and its proposed approach is something that is needed. The project proposes to accelerate the understanding and technology development necessary to address many of the remaining limitations in fuel cells. It is a good mechanism to define, consolidate, and make available the resources at national laboratories to those in industry and academia. However, at face value, it can seem like just another mechanism to funnel money to national laboratories. The project team should include more universities in the funding to help address this perception.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The work to understand degradation is good. While the comparison of low-surface-area carbon and high-surface-area carbon does not show any surprises, the PtCo vs. Pt work is interesting and useful and will lead to increased understanding. It is important to link the results to modeling. The vertically aligned and porous Pt nanowire work was interesting, but the justification and feasibility for the work was not fully explained. The full characterization of the Toyota Mirai structures is very valuable, and this type of work should be continued when possible. Combining the field testing results with the accelerated stress test (AST) results was particularly effective. The modeling approach and results continue to make good progress and are focused in important areas. The effect of heterogeneities is critical and useful. The comparison of the differential cell to the modeling results and understanding differences to integral cell results are useful. The project is starting to correlate a model system for thin films with observed behavior in situ. Studying the solvent effects on inks is valuable. Understanding the inherent pH of the Nafion and how this affects the ink should lead to increased understanding and improved ability to process inks. The conditioning work is important and useful and is starting to reveal some important effects between catalyst types.
- The project team has demonstrated an in-depth analysis of membrane electrode assembly (MEA) component performance and durability aspects. A detailed understanding of the fundamental phenomena will be key to guiding future developments.
- The project team studied platinum, platinum alloy, and carbon degradation and revealed an increase in the local transport resistance. It would be relevant to return the ionomer and membrane to its original proton form to assess the relative role of the Co on ionomer conductivity and oxygen permeability in comparison to the increase in catalyst nanoparticle size. In addition, the team obtained impedance spectra with air and 21% oxygen and 79% helium for that series of tests. It would have been more informative to also obtain data with oxygen to isolate the ionomer transport contribution. Finally, it was observed that at the beginning of life, the mass transport limitations are larger for the alloy catalyst than for platinum. This observation could be the result of a smaller platinum active area (similar in effect to a lower platinum loading with Co covering Pt active sites). This hypothesis is consistent with the presented electrochemical surface areas for the different catalysts. Mathematical modeling was used to analyze several topics including oxygen transport in thin ionomer films and catalyst layers, liquid water transport in gas diffusion layers (GDLs), and cell (integral) performance. However, it is unclear if the flooding of the catalyst layer was observed to provide relevant parameter values for the model (there is apparently no direct evidence of liquid water, either as a film or as distributed droplets). A similar observation applies to liquid water transport in the microporous layer cracks. These observations are consistent with cell model discrepancies for a high value of the relative humidity. The project team designed, built, and tested two new catalyst layer structures. However, the mechanical integrity must still be improved to clearly show the potential benefits. There is a significant amount of risk associated with the proposed structures. Toyota Mirai components were characterized to provide a comparative benchmark. Additionally, the project team assessed the impact of conditioning on initial performance for several catalysts which demonstrated its importance. The characterization was limited to the catalyst and carbon support. It is recommended that the project consider ionomer characterization as well because changes are also expected considering, for example, the relatively larger sulfonate group mobility. The transport resistance measurements appear to confirm this hypothesis. The project team investigated the effects of the catalyst ink composition and processing. Also, the team studied the transport of cations within a cell and thin films, either originating from platinum alloy corrosion

or added to the ionomer and/or membrane to scavenge hydrogen peroxide and radicals. It would be more appropriate to investigate ionomer thin films on more relevant materials such as platinum and glassy carbon rather than gold and silicon/silicon dioxide, especially because substrate effects were observed.

- The accomplishments of FC-PAD have been satisfactory to this point. The greatest impact has been with regard to the development of the complex models using input from industry and academia. The development of a detailed model that can be made accessible to the general scientific public at large and can easily be tuned to fit a broad range of systems would be a great step forward. There has been significant progress made in the analysis of materials, specifically the Toyota Mirai components. However, there should not be too many resources devoted to reverse engineering.
- The project's accomplishments and progress are effective. The project clearly addresses the DOE targets in terms of performance and durability of MEAs and their components. The high number of results is reflected in the numerous publications and presentations and the quality of the different awards received. However, as there are so many results, they need to be well structured within a one-hour presentation in order not to be flooded. Therefore, the presented results should refer explicitly to the associated "Progress Measures, Milestones, and Deliverables." This year focused on PtCo alloy catalyst degradation and the carbon corrosion. The team presented interesting results on ordered array electrodes, but more details on the structures and their properties would have been appreciated. Some durability testing is missing. The second main focus was on the characterization of Toyota Mirai MEAs after 300 hours and 3,000 hours. The presented results are very informative for the community, with some unique structures (big Pt particles, F-enriched layer between catalyst layer and membrane). The project team did not mention any degradation between both MEAs, indicating that Toyota's mitigation strategies are very effective (but no pictures after 3,000 hours have been presented). However, the porosity between 29BC and after 300 hours has evolved, but the project team provided no explanation. It was unclear why the evolution of the hydrophoby of the GDL has not been investigated. Applying current AST protocols on the 300-hour-tested MEA leads instead to severe degradations. This leads to questioning whether the only reason this is done is system strategy management, as claimed. Indeed, it might be interesting to investigate the impact of the MEA structure not only in investigated AST protocols but also in automotive drive cycles. This also raises a question about the relevance of the existing AST protocols and whether they are still adapted to current MEAs or whether some should be updated.
- The project team did not generate many useful insights regarding carbon corrosion, catalyst stability, electrode structure, impact of preparation methods, or conditioning on performance. Modeling efforts support the understanding of fundamentals, as well as observed data. However, the project lacks an explanation as to how those findings contribute to overcoming the outlined barriers.

Question 3: Collaboration and coordination

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

- Regular meetings occur between the five national laboratories and the four awardees (3M, General Motors, United Technologies Research Center, and Vanderbilt University). FC-PAD also has interactions with 20 other organizations (materials suppliers and institutions with specific characterization methods and mathematical modeling capabilities) and receives input from the U.S. DRIVE Partnership and other advisory panels.
- The project coordination approach is very structured for a large project that involves multiple research partners. The collaboration with many additional partners from academia and industry further enhances the consortium's capabilities and supports dissemination of the results.
- The work is well coordinated and cohesive with good communication between groups. FC-PAD is also supporting the funding opportunity announcement (FOA) projects.
- Many of the most renowned institutions, from both academia and industry, contribute to the project. The efforts and collaboration between institutions are well orchestrated.
- The collaboration between the different partners is well structured, well managed, and very efficient.
- Collaboration within and across the national laboratories within this consortium is adequate. The inclusion of industry and academia is limited to the four funded projects. The project team should develop a mechanism to make these resources more accessible and to include more collaboration with academic partners, through more FOAs or some other process.

Question 4: Relevance/potential impact

This project was rated **3.5** for its relevance to/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.

- Durability and performance are the most critical technology areas in which to continue to improve understanding. The linkages of durability with performance are intrinsic to the overall MEA structures and mechanisms being studied, and are absolutely essential to further elucidate driven-down costs. The focus on PGM-catalyst-based MEAs is also the appropriate focus, but projects that focus on catalysts alone are necessary but not sufficient. PGM catalysts at the target loadings under study will be the technology focus for many years to come. It should also be noted that the structures being studied under FC-PAD are not yet commercial and are at low TRL levels, as appropriate for this type of research. When the questions that they are investigating have been answered, and mitigations developed, industry will then—and only then—have the capability to implement results into cost-competitive products. The work that is being done is effective and, for the most part, are the most impactful activities that could be selected at the appropriate level of pre-competitiveness while making effective use of FC-PAD skill sets and considerable facilities. The work is very useful and critical to supporting industry in efforts to reduce costs to make fuel cells truly competitive.
- FC-PAD, as is true of the other existing consortia, is crucial for the Fuel Cell Technologies Office and represents a very high potential to significantly advance DOE in achieving Multi-Year Research, Development, and Demonstration Plan targets. The main targets are improving fuel cell durability and performance while decreasing the cost through a better understanding of the mechanisms involved, leading to a better mitigation solution. The high number of publications and presentations allows a very good diffusion of the knowledge learned to the fuel cell community. This kind of project fits very well with DOE’s evolution toward lower TRLs.
- Understanding the basic fundamentals regarding MEA component performance and durability is very important to enable further component optimization to achieve DOE targets.
- The problems being addressed and the proposed approaches are very relevant to the key limitations of fuel cells. If more input from academic and industrial partners is included, the potential impact and pace of addressing these goals could be increased.
- FC-PAD is focused on two (performance and durability) of the three Hydrogen and Fuel Cells Program objectives (cost being the third objective).
- In-depth understanding of the interactions on a nanoscale is being developed, which is necessary in overcoming the fundamental barriers. However, it is not made clear how the single efforts and findings can contribute to optimizing performance or durability.

Question 5: Proposed future work

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

- The proposed future work is well planned and appropriate. It is important to continue to investigate different models for the ionomer thin film and local oxygen transport mechanisms. The project team should include further justification of the arrays and nanowire work, with clear go/no-go decision points on that work. FC-PAD should continue to work on material sets as it has planned, despite the fact that system mitigation solutions are available. System mitigations result in higher costs to the overall product, and improved materials are essential to bring costs down.
- The future work is very detailed, and it is clear how the project team proposes to address the indicated problems.
- The proposed future work is reasonable to further develop the understanding of the fundamental phenomena. The testing of state-of-the-art components that has been presented for components of the Toyota Mirai should be continued to develop a benchmarking standard for MEA components. This, of course, depends on the availability of state-of-the-art materials and whether it is possible to publish the results.

- The future work activities proposed are relevant and appropriate. However, the project team should propose better-quantified milestones. Regarding the results obtained from the Mirai's MEA analysis, the questions raised on the singularities observed, and the relevance of catalyst AST, the investigation should continue next year and even be extended to other "real-life" aged MEAs.
- The future work proposals address important aspects in further understanding the mechanics of the cathode. However, the work packages seem rather unspecific.
- For ionomer thin films, it would be more beneficial to use a platinum substrate instead of carbon, considering the relatively more important oxygen mass transfer resistance in comparison to the ionomer proton resistance. For water management, the project team mentions water visualization in various components. It is recommended that the project initially focus activities on hypothesis confirmation (water imaging in catalyst layers, preferably at the pore size level, water transport in microporous layer cracks).

Project strengths:

- The project has a comprehensive and cohesive effort focusing on most critical areas to understand and therefore provide the ability to mitigate performance and durability shortcomings in PEM technology. The team is systematically studying well-prioritized areas. The project incorporates strong experimental characterization tools and modeling approaches. The characterization of the Mirai structures is a new area that is incredibly valuable. This is an excellent team of the highest caliber.
- The project includes efforts from all major U.S. institutes and many important companies and therefore has a broad knowledge base and access to materials, analytic capabilities, and experience. Industry partners can reflect the necessities and problems under operating conditions. The project addresses the right problems to eventually overcome the described barriers.
- The project demonstrates the development and accessibility of the top characterization equipment and processes. The project has improved insight into the issues limiting fuel cell performance and durability. The team has developed a model that encompasses all of the processes and length scales to highlight potential solutions.
- The project has collaboration between multiple laboratories and a combination of individual strengths and capabilities. There is a strong focus on publication of the results in a large number of publications. The project team has a very valuable knowledge base for the further optimization of MEA components. Developing a kind of design guideline that provides a summary of the project's findings might be considered. A high-level executive summary of the project's results would be helpful for a fast overview of the findings.
- The multiple lead investigators are of an excellent level, and the consortium is gathering the national laboratories' core competencies and the associated huge amount of equipment. The work is conducted in a structured manner, with extensive characterizations.
- The project strengths include experimental characterization and mathematical modeling capabilities; coordination between FC-PAD members, stakeholders, suppliers, and collaborators; and focus on fuel cell performance and durability.

Project weaknesses:

- There is a limited number of FOA-funded partners and a limited scope of contamination studies. The mathematical model is based on liquid water transport parameters that is not directly measured. There is a perceived fragility of the proposed ordered array catalyst layer structures and an absence of ionomer characterization for conditioning studies. Another project weakness is the substrate choice for ionomer thin film studies.
- Although it has already been discussed and addressed in previous reviews, the focus on only the MEA components limits the performance and durability results somewhat. It would be good to provide more insight in the testing hardware for the in situ tests (especially details of the test cell/flowfield) to enhance the ability to interpret the results. In the past, the flowfield design could have a very significant impact on cell performance results, even for differential cells.
- As a consequence of the large number of activities, the project lacks a clear and understandable summary of the results of the year, how the results are positioned toward the global objectives of the project, and how the results will affect further industrial developments.

- The project needs further integration of input and funded collaboration with academia and industry to show that this is not just a mechanism to funnel money to the national laboratories. The team should focus on reverse engineering.
- The individual work packages and findings should more clearly address how they contribute to optimizing electrodes and MEAs and overcoming the defined barriers.
- The slides could have better diligence on defining experimental details and materials sets to which the data refers.

Recommendations for additions/deletions to project scope:

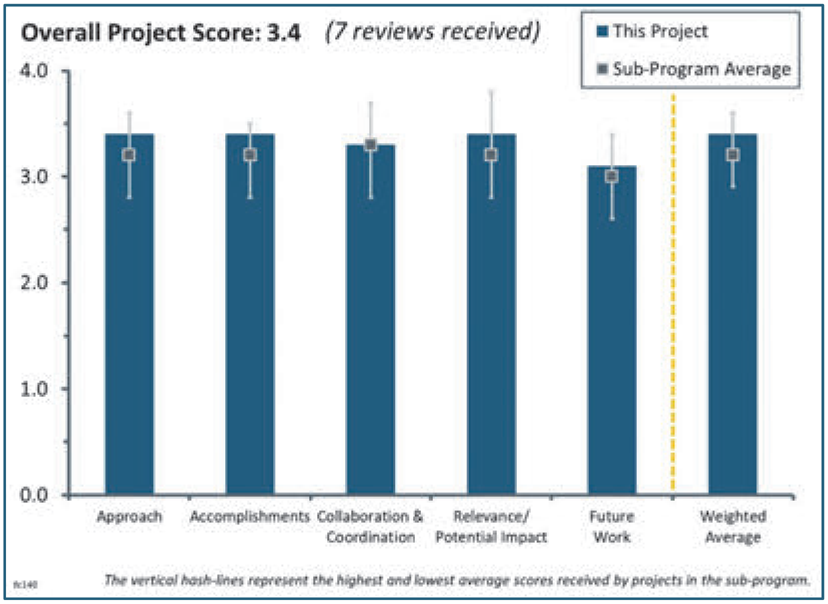
- The project team should further investigate the discrepancy between the AST protocol results and the Toyota Mirai testing results. It is true that the target of the AST protocols is to develop an understanding of fundamental phenomena on the materials side. However, special attention should be paid that the materials are not “over engineered” to achieve the best performance in the AST protocols when alternative, lower-cost approaches could meet the requirements of real-world applications. Based on the know-how gained from real-world operation of the latest vehicles, the team should develop a second set of test protocols that can be used by materials developers to optimize their materials. (As an example, there are trends where too-harsh ex situ testing conditions for coatings of metallic bipolar plates did not reflect the performance in real in situ operation.) The extension of the state-of-the-art testing to additional materials and documentation of the material’s results in scatterbands would be great. Of course, this requires the “okay” from the manufacturers, but if the FC-PAD team can discuss with other original equipment manufacturers and qualify materials similar to Toyota’s, that would be very helpful for the overall development. It might be worthwhile not only to address degradation phenomena but also to develop approaches for regeneration strategies, if possible. The work on activation and break-in procedures is very important. The project team should pay special attention to this because a short and efficient break-in procedure will be key for low-cost, high-volume production of automotive fuel cell stacks, where stack conditioning time is one important cost driver.
- The results could state more clearly the impact on the key performance indicators. It would be helpful if the findings could be transformed into design rules in order to facilitate optimization. A reference system (e.g., MEA, operating conditions, standard measurements) could be defined, which then could be used to demonstrate whether the findings can be translated into an optimization of performance or durability.
- The project team should improve the timelines and the quantitative description of milestones. The presentation for the review should be provided in time in order to enable the reviewers to work on it adequately before the Hydrogen and Fuel Cells Program Annual Merit Review.
- The project should incorporate more funded collaborations with industry and academia and limit the effort associated with reverse engineering of commercial materials.

Project #FC-140: Tailored High-Performance Low-Platinum-Group-Metal Alloy Cathode Catalysts

Vojislav Stamenkovic; Argonne National Laboratory

Brief Summary of Project:

A primary focus of the U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program (the Program) is development of highly efficient and durable Pt alloy catalysts for oxygen reduction reactions (ORRs) with low Pt content. This project will go from fundamentals to real-world materials to achieve rational design and synthesis of advanced materials with a low content of precious metals. Researchers are taking a materials-by-design approach to design, characterize, understand, synthesize/fabricate, test, and develop tailored high-performance low-Pt-alloy nanoscale catalysts.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The proposed technology is based on the well-established materials-by-design principle, which includes design of material, characterization, evaluation of electrochemical performance, and analysis of the data. The principal investigator (PI) clearly emphasized both project objectives and existing critical barriers. Overall, the project description is easy to follow. The targets and methods of the project team's accomplishments were rationally selected according to the DOE requirements. The project integrates relevant effort and is feasible based on the progress reported.
- The overall approach is excellent, covering development, characterization, and small-scale fabrication of platinum-group-metal (PGM) ORR electrocatalysts. The development of catalysts is based on translating materials and knowledge developed on well-defined systems (single crystals and thin films) to practical nanoparticles. The inclusion of small-scale production is especially relevant, as effective catalyst design also needs to be compatible with practical fabrication methods.
    - Argonne National Lab's (ANL's) characterization is directly relevant to meeting project objectives, and the project team has many unique and unmatched capabilities. The increased focus on membrane electrode assembly (MEA)-level testing is critical for understanding limiting factors and is therefore appreciated.
    - One aspect of the approach that could use improvement is inclusion of work specifically aimed toward understanding the factors responsible for the circa 10x (or more) reduction of catalyst mass activity when translating from rotating disk electrode (RDE) to MEA. It is unclear whether ionomer adsorption is alone responsible or other factors are responsible (e.g., catalyst degradation in the MEA). The resolution of this issue would substantially increase the operating efficiency of polymer electrolyte membrane fuel cells (PEMFCs) and increase commercialization probability.
    - ANL is also continuing the development of the porous and hollow catalysts. While extraordinarily active in RDEs, the team will need to assess the characterization for activity and durability in the MEA. It is unclear whether such highly engineered structures can remain intact after MEA evaluation, including accelerated stress tests (ASTs).

- ANL has an excellent organization of efforts, with clearly defined tasks and roles for each national laboratory partner to contribute to a common objective.
    - The intent of associating catalytic function and performance with microstructures and compositions should be the best means for developing comprehensive insights into the fundamental mechanisms. Ultimately, this path should lead to solutions for maximizing the efficiency of the catalysts to reduce costs of fuel cell MEAs. It is not fully apparent in this presentation just how far this project has gone toward its initial objectives.
- The approach is excellent. The RDE-inductively coupled plasma mass spectrometry (ICP-MS) measurements of catalysts with scale-up, and real fuel cell measurements against baseline materials, provide credibility.
- ANL used conventional wet chemistry to synthesize highly dispersed Pt nanoparticles deposited onto carbon support. ANL's approach of first synthesizing Pt nanoparticles and then supporting these nanoparticles on high-surface-area carbon resulted in high Pt surface catalysts with a high electrochemical surface area.
- ANL has an excellent materials-by-design approach and very good coordination among the partners and laboratories.
- The approach is very scientific and well defined.

Question 2: Accomplishments and progress

This project was rated **3.4** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team successfully synthesized different monodispersed nanoparticles with uniform compositions. The team also demonstrated synthesis of Pt_3Au nanoparticles on carbon support to obtain almost zero Pt dissolution and highly stable Pt catalysts above 1.2 V.
    - ANL has demonstrated scaling up of various catalyst architectures (e.g., nanopinwheels, nanocage) without performance loss or particle agglomeration. The comparative particle size and distribution between the catalysts made through batch method and flow reactor for high-speed production is commendable (slide 19). The retention of an original monodispersed catalyst structure with a large-scale synthesis method is a great accomplishment.
    - The team also proved the versatility of their synthesis process. They have demonstrated the method with different supports and loadings capable of controlling the catalyst active surface area. This helped the team to achieve high mass activity of 500 mA/mg_{Pt} with a PtNi catalyst. The catalyst also performed almost two times better compared to the commercial catalyst from TKK.
    - The team demonstrated a PtCo intermetallic alloying method to make a catalyst with Vulcan carbon support to improve Pt and Co dissolution and achieved 700 mA/mg_{Pt} with a PtCo catalyst. Overall, the team demonstrated the flexibility of their catalyst synthesis tolls to make a monodispersed low-loading catalyst with high mass activity that has the potential to meet DOE's 2020 performance targets.
- The team of ANL, Oak Ridge National Laboratory (ORNL), and the National Renewable Energy Laboratory (NREL) achieved excellent progress in all tasks (Tasks 2–5). The PI summed up these tasks and shared them with the community.
    - The project team demonstrated the accomplishments that had been experienced on several levels (as it was originally proposed by Dr. Stamenkovic): (1) an understanding of the fundamental origin of intrinsic ORR activity of Pt and PtM catalysts, based on preferential exposure of crystallographic planes, (2) the selection of nanostructures enriched with these facets (shaped nanopinwheels), (3) the synthesis and scale-up, and (4) the comprehensive analysis (physicochemical), followed by fuel cell tests. For 1-3, either the critical barriers were addressed, or the selected pathway will unambiguously result in the successful meeting of all DOE targets, with outstanding results (the preservation of shape and connectivity in Pt-structure with batch size increased from 0.1 to 3–5 g).
    - Taking into account a completely different integration of shaped nanoparticles on non-specifically designed supports into the MEA structure, the progress in electrochemical evaluation is excellent. It demonstrates coordinated teamwork between members of this project. The electrochemical activity of the catalyst (measured at high potentials) is at least two times higher compared to commercial Pt/C catalysts, while the loading of platinum was decreased to 0.03 $mg(Pt)/cm^2$. The overall demonstrated progress excludes any doubts of how the team addressed critical barriers to achieving DOE goals (listed as milestones and go/no-go points in the project).

- The team has continued to make excellent progress meeting the project's catalyst objectives, which are well aligned with DOE goals. Along with demonstrating the high activity of new catalysts in RDEs, which exceed the DOE target by >10x, the team has made good progress in demonstrating the scale-up feasibility of several project catalysts.
    - The team has made good progress toward integration of project catalysts in MEAs. The additional focus on the integration of the catalysts into high-performance electrodes/MEAs that are capable of demonstrating performance approaching entitlement is warranted.
- This is almost the end of the project. The team developed many high-ORR active catalysts, which showed excellent results in RDEs. The team introduced the MEA tests pretty late in the project. If the project team had introduced MEA tests earlier, it could have helped in designing or modifying existing designs and composition of developed catalysts to make them work better in the MEA. The MEA data shown with very low Pt loadings (around 0.03 mg/cm^2) is very impressive.
- The project has exceptional synthesis of novel materials and scale-up.
- The scale-up and fuel cell performance is a major accomplishment of this project.
- Although extensive characterizations were performed, and testing indicates some properties were improved in the test samples, there was no clear indication of how much direct progress had been made over the past three years of effort toward MEA milestones.

Question 3: Collaboration and coordination

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

- Despite having world-class expertise in designing shaped nanoparticles as well as characterizing and evaluating fuel cells, the team established several important inter- and intra-institutional collaborations that provide substantial benefits for the success of the whole project. Those collaborations included practically all national laboratories participating in the fuel cell effort, a number of small U.S.-based businesses, and, recently, the research and development centers from automobile OEMs.
- The team has good collaboration between the three national laboratories: ANL, ORNL, and NREL. ANL has extensive catalyst synthesis and characterization expertise, ORNL has extensive catalyst-coated membrane (CCM)/MEA characterization expertise, and NREL has expertise in CCM/MEA and fuel cell testing. The collaborators are all complementary to each other, and together, they have all the expertise and resources needed for carrying out the proposed tasks in this project.
- This project has excellent collaboration between ANL, ORNL, and NREL on synthesis, analysis, and MEA testing, respectively. The team should approach other laboratories, institutes, and/or industry to test the active catalyst in the MEA once the scale-up issues are sorted out.
- The level and types of collaboration are good. The collaboration is appropriate for a catalyst development project, including apparently increased collaboration on MEA-level testing and diagnostics. Additional collaboration with state-of-the-art original equipment manufacturer (OEM) catalyst and electrode developers would be useful, as OEMs could potentially increase the probability of demonstrating relevant performance in MEAs.
- This project appears to have a high level of cooperation with the group of national laboratories. It is less clear whether interactions with outside groups of OEMs were very active.
- The partners are only national laboratories; these materials need to get into the hands of fuel cell system manufacturers or MEA manufacturers. This will flush out any remaining technical challenges with these materials.
- This project needs more collaborators other than national laboratories.

Question 4: Relevance/potential impact

This project was rated **3.4** for its relevance to/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.

- The relevance of the project is outstanding. The team is directly addressing key fundamental activity, cost, and durability barriers that are critical to enabling further commercialization of PEMFCs. No other PI or catalyst research organization has the breadth of expertise and capabilities demonstrated by this project.
- The PI emphasized the relevance of the proposed technology to the DOE mission during the Program Annual Merit Review meetings. ANL has already demonstrated the impact: the critical step of scaling up highly active (but at the same time possessing high surface free energy) nanostructures to TRL 2–3 (up to 5 g), in combination with an impressive intellectual property portfolio (11 in total), resulted in OEMs' interest to the technology. The team successfully supports and advances progress toward Program goals and objectives.
- The impact to the field can be enormous. The scope of work directly addresses performance, cost, and durability targets.
- The project targets are all relevant to DOE's 2020 targets. The team has focused very carefully on achieving DOE goals and has designed the tasks accordingly.
- The potential impact of these new catalyst materials appears to be high, particularly with the major boost in fuel cell performance in the laboratory environment.
- The project does align well with DOE's hydrogen fuel cell research direction for low-PGM catalyst development. To meet DOE 2020 targets, the project team would need greater efforts to evaluate high-current-density MEA challenges of low-PGM catalysts.
- Although the project team presented numerous images of support catalysts and the tests indicating improvement of various parameters, such as voltage, the actual progress for meeting the DOE MEA targets with lower concentrations of Pt-based catalysts was not apparent. In particular, it was unclear what the expected behavior would be, based upon the "best" materials identified during the three-year course of this project. There was no evidence of any major advances having been made.

Question 5: Proposed future work

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

- The future work plan is directly relevant to addressing key fundamental barriers for PGM ORR electrocatalysts, but current funding is set to expire this year. It would be good for the work to continue, especially the resolution of the MEA integration challenge of activity loss.
- The project is coming to an end in October 2018. The future work, broadly described by the PI on slide 30, is relevant to the development of high-performing, low-PGM loaded catalysts. The team may pursue this work with future funding.
- The proposed plan on the remaining budget period is well justified and will cover the team's remaining deliverables, according to the original statement of project objectives.
- Since this project ends in October 2018, there will not be much more additional work performed, other than completing current tasks and writing the final report. The authors should thoroughly and explicitly document what was found to enhance the performance of the studied Pt-based catalysts. In particular, they should note whether these studies led to substantial reduction of the quantity of catalyst needed to yield MEAs that could achieve DOE performance levels.
- The team should include durability in operating fuel cells in the future work. Although the RDE coupled with ICP to look at Pt dissolution was novel and clever, it is not clear whether it has any correlation to real fuel cell system durability. Thus next steps should include performing an AST on MEAs made with the new catalyst materials.
- The future work should be prioritized for resolving surface chemistry in the MEA and simultaneously scaling up in grams (to at least the 5 g level) so more MEA evaluations can be done. Alternate approaches for catalyst synthesis should be lower in priority compared to alternative supports, which may result in more improvements in MEA for high-current-density performance.
- The project's future should include fuel cell testing of materials.

Project strengths:

- This has been a highly coordinated team of experienced researchers from several national laboratories utilizing specialized experimental capabilities focused on the common objective for improving performance of Pt-based catalysts. The team produced a variety of Pt-based catalysts and characterized their dimensions and composition extensively.
- The team has demonstrated new catalyst materials that show good promise of bringing down PGM costs. The scale-up and fuel cell performance data are key to demonstrating the potential of the research.
- The team has an unparalleled fundamental understanding of ORR catalysis from theory to materials fabrication and characterization. The team has a focused effort on limited scale-up.
    - Another project strength is the demonstration of catalysts with more than ten times the DOE target for mass activity.
- The input into understanding the correlations between the performance of Pt catalysts measured in RDEs versus MEAs has a substantial impact on the fuel cell community. The proof of concept in highly durable nanoparticles, as well as in well-defined Pt alloys (intermetallic systems) that can be scaled to feasible amounts, is impressive and is definitely a breakthrough in the field. The series of PtNi and PtCo with multilayered Pt shell and novel nanopinwheel structures already exceeded the DOE 2020 technical target for mass activity in MEAs.
- This project has a great team. This is a good ensemble of expertise and technical resources to work on such a complex project.
- This is an excellent team of researchers from ANL, ORNL, and NREL, with an excellent materials-by-design approach. Many high-ORR active catalysts have been developed, characterized, and tested.
- This project has made significant progress in producing a novel catalyst, as well as the ability to scale up.

Project weaknesses:

- According to the presented progress, demonstrated accomplishments, and impact on the field, programmatic weaknesses are insignificant. Several minor optimizations in the scale-up tasks that could result in higher yields (~15%) definitely should be considered as continuation of scientific discourse and cannot be considered as impeding project success.
- The project team should include more MEA evaluations at an earlier stage of the project to provide feedback to the catalyst design. The RDE is an excellent tool, but there is too much dependence on RDE data to judge the catalyst viability; this could be tricky. The project team could have prioritized the scale-up efforts with the help of a catalyst supplier's feedback.
- The primary project weakness is that electrode optimization efforts are likely not sufficient to achieve entitlement performance with these high-activity catalysts. Additionally, the project needs more characterization of catalyst composition and structure after MEA testing to assess degradation modes.
- No summary evidence was provided that demonstrated any significant improvements in reducing Pt contents while meeting or achieving the performance targets for subsequent MEA devices resulting from this project. While several electron microscope images of embedded Pt clusters were presented, the correlation to reaching the performance levels was not shown.
- The project was heavy on catalyst design, synthesis, and electrochemical characterization, but it did not have much on in situ fuel cell characterization or any fuel-cell-system-level characterization.
- The project is missing fuel cell durability data and collaboration with industry.
- The project needs industry input.

Recommendations for additions/deletions to project scope:

- Since this task is ending within a few months, there is no need to alter project scope. However, the team should clearly identify what processing steps led to improved behavior from the catalysts. The team should also fully document all issues and approaches that did not succeed.
- The project should be extended to enable additional ORR catalyst development with specific focus on determining and resolving the mechanisms for deactivation in MEA electrodes as compared to RDEs.
- The project's remaining timeframe does not allow time to propose additional sub-tasks to the project scope; however, the proposed future activity is well designed and balanced.

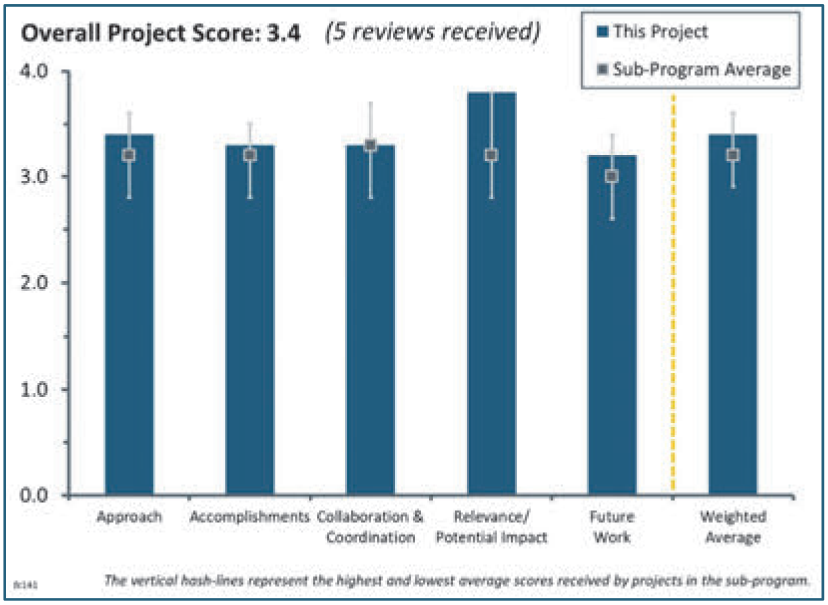
- The project is successfully ending soon. If there is any next phase, then more scale-up and MEA tests to meet high-current-density targets would be great. The team has already met loading targets.
- The team should focus more on collaboration with industry; however, the project is ending in four months.
- The project should be continued.

Project #FC-141: Platinum Monolayer Electrocatalysts

Jia Wang; Brookhaven National Laboratory

Brief Summary of Project:

This project aims to synthesize high-performance platinum monolayer electrocatalysts for the oxygen reduction reaction consisting of a platinum monolayer shell on stable, inexpensive metal, alloy, metal oxide, nitride, or carbide nanoparticle cores. Three low-platinum catalysts will be developed that will meet the U.S. Department of Energy technical targets for 2020.



Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project focuses on improving catalyst durability and performance by using advanced core–shell nanostructures with various synthesis and processing methods.
- The approach in this project was well placed, which is justified by the outcome.
- The catalyst synthesis strategies and compositions that the project team are developing are interesting considering the excellent rotating disk electrode (RDE) results. However, the project team should put more effort into fundamentally understanding why the mass activity is so much lower in the membrane electrode assembly (MEA) tests versus RDEs.
- This project started with a very broad approach to core–shell catalyst design and has converged on a few approaches. The range of topics is still quite diverse, but the project has made intriguing discoveries that may merit more focused study. For example, it is argued that the Pt/NbO catalysts have a specific morphology, but evidence for this morphology is lacking.
- The approach targets the most critical aspects of platinum-group-metal (PGM) catalysts (high electrochemical surface area (ECSA), reduced PGM content, and scale-up to MEA-relevant quantities). However, it is clear that further MEA design was warranted in the project, as MEA ECSA was vastly inferior to RDE results, the 0.2 mg/cm^2 baseline showed oddly poor performance, and the MEA data were poorly interpreted.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project has shown excellent RDE results with several varieties of catalysts and promising initial results in MEAs at low current density. Considering electrode optimization was not the focus of the project, the catalyst-specific results were very good.
- The principal investigators achieved significant progress in this project by introducing a number of highly diverse systems. Electrochemical evaluations in RDEs showed great performance, and promising catalysts were synthesized to multiple gram amounts. In addition, the team performed an MEA test to address DOE technical targets. Despite very promising RDE evaluations, it is apparent that catalyst performance in the MEA was not at the expected level, and the DOE target for mass activity was not achieved.

- The team carried out investigations on five electrocatalyst designs, and the results were clearly stated. The performance results by RDE were supported by MEA testing for selected structures.
- The project has delivered proof-of-concept studies with performance data and some scale-up on a range of catalyst designs.
- At the RDE level, only the PtNiN/C catalyst appears promising. The other catalysts all have either low mass activity or low ECSA. Also, the summary table on slide 15 does not include ECSA. This is odd, as General Motors (GM) is a partner on this project and has been a strong proponent of the importance of ECSA for any catalyst targeting PGM loadings of ≤ 0.1 mg/cm^2.

Question 3: Collaboration and coordination

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

- The collaboration with the participants in this project was coordinated in an excellent manner.
- Good collaboration appears to exist between the partners, industry, and academia, and the studies are coordinated well. However, the contributions from partners are not always explicitly stated.
- At the catalyst level, the project showed strong collaboration. However, it looks like only limited collaboration was achieved with MEA integrators. As MEA integration is such a critical aspect of this project, the project probably warrants more involvement from GM/Toyota.
- There seemed to be appropriate partner organizations on the project. It was difficult to determine whether all of the collaborators contributed significantly based on how the data were presented. It seems that stronger collaboration on MEA synthesis would be beneficial, as it was not clear how much effort MEA partners put into optimizing MEA preparation.

Question 4: Relevance/potential impact

This project was rated **3.8** for its relevance to/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 highly relevant to DOE’s PGM targets, and further investment in this line of work is strongly recommended.
- The project points the way for a number of catalyst concepts, including the potential for scale-up. Industrial partnership increases the potential impact.
- The project scope and goals align well with DOE objectives on catalyst performance and durability for fuel cells.
- The project is advancing the development of novel catalyst compositions that show promise for addressing key catalyst technology challenges.
- This project is one of a few that has very high impact on the DOE Hydrogen and Fuel Cells Program (the Program).

Question 5: Proposed future work

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

- This is the last year of funding for this project, and proposed future work is reasonable for the amount of time left.
- Future work tasks, such as MEA testing/optimization and scale-up, are key to achieving the project objectives.
- The catalysts appear to have intrinsic activity, so it is not necessary to further improve activity. The focus should now move to MEA testing/optimization.
- The proposed work follows logically from current accomplishments. The final studies of this project should focus solely on MEA-scale performance and durability. The proposed PGM-free work is intriguing but not within the scope of this project.

- The project should move forward with the proposed work on core–shell catalysts; the team should not switch the focus to PGM-free catalysts. This group has already made great progress with PGM catalysts (particularly the PtNiN/C catalyst). The team should stick to its strengths. While promising, much of the PGM work shown at this Program Annual Merit Review (including the current project) is at a very low technology readiness level (2–3). Thus, it is too early for industry to get involved, and further funding is necessary to advance this critical work.

Project strengths:

- The project can be viewed as one of the most valuable efforts funded by DOE and the Fuel Cell Technologies Office. The outcome from this effort is a long list of highly diverse Pt-based systems that can be readily applied to the MEA. The main value from this effort is correlation between fundamental properties and functional behavior of catalytically active systems.
- Brookhaven National Laboratory is continuing to produce exciting, next-generation core–shell catalysts that will likely be a core technology in the coming years. The goals of this project are fully aligned with some of the key current bottlenecks to polymer electrolyte membrane fuel cell commercialization.
- This project has good partnerships with industry, the national laboratories, and academia. The results and progress are summarized well, and the team has made good progress toward scale-up and MEA testing. The team has produced a good set of publications.
- This is, thus far, a fruitful project that has led to important discoveries of techniques for core–shell catalyst design, manufacture, performance, and durability. The Co nanowire morphology and NbO_x approaches are particularly intriguing. The results provide a strong platform for future detailed study.
- The project is developing interesting catalyst compositions with promising intrinsic activity and durability.

Project weaknesses:

- The broad range of studies presented limits the ability of this project to go into detail. In particular, a more detailed discussion of the Pt/NbO morphology would be of interest.
- The MEA integration activities were disappointing. More work needs to be performed here to understand where the large discrepancy in ECSA originates. Also, ECSA should be included in any future summary catalyst, as this is a critical parameter for high-current-density operation.
- The activity and performance results are not transferring to MEA testing.
- This effort has not yet delivered a high-performing catalyst that can achieve or exceed DOE technical targets simultaneously.

Recommendations for additions/deletions to project scope:

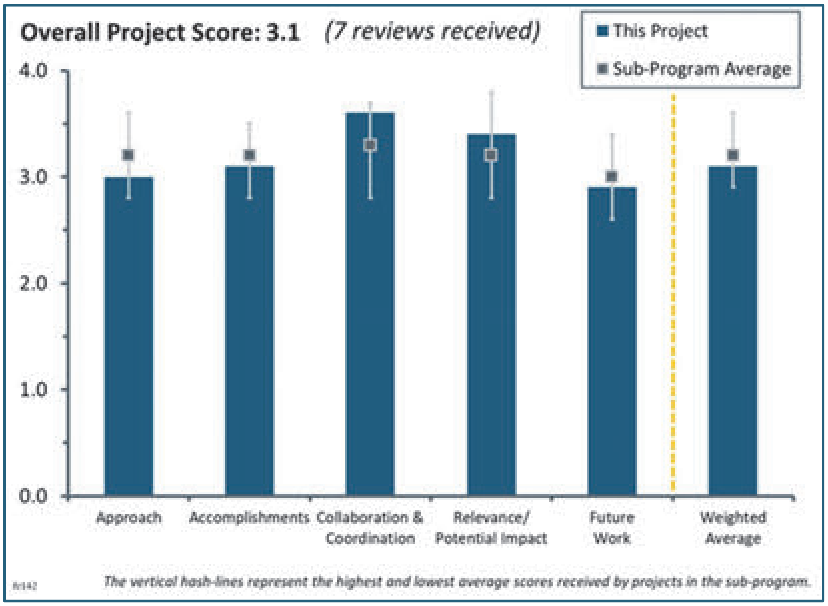
- The project team needs to continue toward simultaneous improvement in durability and activity of promising structures supported by scaling up and MEA optimization.
- The project should not focus on improving intrinsic activity and/or RDE testing any more. Instead, the focus should be on improving MEA results or understanding why the results do not match the state-of-the-art results at the MEA collaborators (GM and Los Alamos National Laboratory).
- For the remaining time in this project, the researchers should focus on effective transfer from RDEs into MEAs.
- The project team should focus on PGM catalysts. It is disappointing to see this team switching focus to PGM-free catalysts.

Project #FC-142: Extended Surface Electrocatalyst Development

Bryan Pivovar; National Renewable Energy Laboratory

Brief Summary of Project:

Platinum catalysis remains a primary limitation for fuel cell commercialization. This project is developing durable, high-mass-activity, extended-surface platinum-based catalysts for decreased fuel cell cost, improved performance, and increased durability. Researchers are focusing on novel extended thin-film electrocatalyst structures (ETFECSs), a particularly promising approach. Parallel efforts include novel extended nanotemplates; atomic layer deposition (ALD) synthesis of platinum–nickel nanowires; and membrane electrode assembly (MEA) optimization and testing including multiple architectures, compositions, and operating conditions.



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 **3.0** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- Using ALD of Pt on Ni and Co nanowire (NW) to make an alloyed low-loading catalyst is a good approach to making stable catalysts. The team has demonstrated their approach on a small scale successfully and is getting good results in large-scale production with ALD. This approach is expected to give a durable catalyst, as the support material is solid NW, which is not prone to degradation as carbon support material.
- Extended surfaces can address many of the limitations of nanostructured Pt catalysts, namely specific activity and durability. The key to the approach is the demonstrated ability to scale the ALD process, potentially to the kilogram scale. The progression of the project to this point and the proposed future work are well aligned to address many of the remaining issues and questions.
- The project has excellent focus on key barriers, including mass-transport limitations at rated power, scale-up, and durability. One durability measure has been met, and the project is close to a second. A pathway to scaled-up and improved rated-power performance is described, but the route to improved durability is not yet clear.
- The work is laid out, and key barriers are identified.
- The overall approach is satisfactory and has resulted in the generation of high-mass-activity catalysts in the rotating disk electrode (RDE). However, it remains to be determined and demonstrated that the overall approach will result in active, high-performance fuel cell MEA catalysts. One primary challenge is that it is unclear whether the ETFECS structure with the hollow core (after dealloying) will be stable against electrochemical cycling, which does not appear to have been assessed to any significant extent (it is mentioned only on slide 24). Another aspect of concern is that there appears to be relatively little MEA testing with exposure to hydrogen/air with state-of-the-art components (e.g., thin polymer electrolyte membrane [PEMs]); this testing process is critical for assessing impacts of residual transition metals. There is also little characterization of structure and composition evolution after fuel cell testing and durability testing.

- The approach has been improved from past years since durability and high-current performance are receiving greater emphasis in the recent milestones. However, electrocatalyst cycle durability would be more valuable to observe than durability to the support corrosion accelerated stress test (AST). The electrocatalyst cycle should have received higher priority. The analysis of durability and mass-transport resistances has been enabled by the removal of excess Ni in the catalyst concept presented last year. The ability of ALD NanoSolutions, Inc. (ALDN) to produce three tons/day was noted by the presenters in the question-and-answer session. It is good to see an approach based upon a catalyst that can be scaled. The project is now over two years old, and there have been opportunities to revise milestones, so it appears late to be addressing robustness, electrocatalyst cycle stress testing, and power densities that extend beyond 600 mW/cm^2. These matters should have been addressed earlier.
- The approach for this project is aimed at developing durable, high-mass-activity, extended-surface Pt catalysts, and optimizing MEA performance and durability for these materials. Two major issues remain. First, the team needs to come up with a verified process, such as the acid-leaching step, to make the MEA fabrication process viable. It is well known in the PEM technical community that any leftover Ni in the electrode will quickly destroy the membrane, significantly decrease cell performance, and affect durability. This project does not define a method for verifying that Ni does not and will not leach out of this catalyst. Second, the mass activity is low, and there is a very large variation from batch to batch. Project modifications need to address process control.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Roughly 70% into the project, the team has demonstrated good progress, meeting performance and batch processing milestones. The researchers have developed methodologies to gain better control of the Ni content in the thin film and have identified more optimal processing and post-processing handling methods to improve activity metrics. The project team has also met the DOE durability target, which has been questioned in the past.
- The team has done well since the 2017 DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR). First, the team has demonstrated catalyst mass activity of >440 mA/mgPt, meeting the DOE target for 2020. Second, the project team has synthesized a large-scale (>5g) catalyst with a high mass activity of >500 mA/mgPt. Third, the acid-leaching step seems to be crucial for obtaining well-performing catalysts; the team has a good handle on this process and has demonstrated batch reproducibility of this step. Fourth, the project team has developed an ALD method for binary catalysts Pt and Ni on Co NW and hence has controlled the amount of Ni in the catalyst well. Finally, the team has demonstrated 5,000 hours of durability, meeting DOE's target of less than 40% performance loss. Overall, the team has accomplished some of the important DOE goals. However, the goal for electrocatalyst durability was not met. The team should investigate whether the loss of mass activity is due to the loss of Pt from the NW surface. Pt loss and its inherent integrity on the NW have not been considered or analyzed by the team.
- The project group understands the pros and cons (e.g., too much transition metal is bad). Mitigation and development is steady. There is a minor issue: progress is confounded by providing polarization curves in A/mgPt. Industry identifies 900 mV for mass activity (for which the team provides data). Polarization curves can be added with current density (A/cm^2) on the horizontal axis. If the team wants to provide H_2/O_2 polarization curves, that is fine.
- Good progress has been made toward demonstrating mass activity, which exceeds the DOE target in MEA, perhaps owing to optimization of oxygen concentration during ALD. Some electrode optimization work has been conducted, showing potentially improved hydrogen/air performance on slide 16. However, the performance still remains quite low relative to state-of-the-art MEAs, and it is unclear whether the underlying factors for the lower performance are understood. Electrocatalyst durability is a key parameter and needs to be significantly improved.
- For 0.1 mgPt/cm^2 cathode loading, hydrogen/air polarization was improved to approximately 0.8 A/cm^2 at 0.6 V (fully humidified, 80°C, 150 kPa). This is still far shy of the 2020 power density target (1 W/cm^2) but does represent progress from the year before. The use of a PtNi to C optimization was a good measure for the project to take to understand how to make the most of the catalyst. Low-temperature performance and

robustness testing is yet to be reported. Electrocatalyst cycle durability needs to be reported. Good mass activities have been consistently shown from various batches with scaled-up catalysts. In general, the project has done well to pay attention to the manufacturing scale possible for the catalyst.
- The project has met all of its milestones thus far.
- Performance is still low. There has been significant progress at the RDE level, but there is a long way to go, and the performance at the MEA level is not nearly as good. In addition, performance variations are very high for both types of testing, suggesting that significant additional efforts on optimization of both the catalyst and the catalyst layer will be required. The authors claim that the "local mass transport is not limiting"; however, the data suggests significant mass transport issues when operating in air.

Question 3: Collaboration and coordination

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

- Key personnel are fully qualified, as demonstrated by the successful completion of previous projects and by the team's publications on work in this and related fields. The proposal clearly and completely defines the roles and contributions of each team member, including financial support from partners. The final team, facilities, and equipment required to complete this project are fully in place, ready, and available. This project has full commitment from the partners' senior management and corporate officers. Ample facilities are available to support and complete the proposed work.
- The team is composed of well-known technical personnel from reputed academia and national labs. ALDN has demonstrated the capability of making ALD catalysts on a large scale. Overall, the task coordination and information/data flow between the collaborators is happening well. The principal investigator is very capable of coordinating tasks between multiple collaborators.
- The fact that the project delivered a no-go decision on a partner whose task did not work out is a positive for the project. More projects should cut tasks in a like manner. The collaboration with ALDN has been particularly effective in answering questions about scaling up the catalyst concept. While it would be a waste of taxpayer funding to fully optimize and engineer scaled-up batches of catalyst within a specified degree of repeatability, the project has done more than enough to alleviate concerns regarding manufacturing scale. Other national laboratory projects have not done nearly as well in representing manufacturing scale. CSM appears to have delivered high-resolution elemental maps of where Pt, Ni, and Co exist in the NW. The project slides could do better in confirming CSM's contributions. CU appears to have discovered preferred ALD routes with 5% O_2 and co-deposition of Pt and Ni. The slides would benefit from making the CU contribution clearer.
- Both the imaging and elemental analysis were good and clearly help the project. The local transport work is good.
- Collaboration, organization, and feedback have been effectively designed and utilized.
- The project team, including Colorado University (CU), Colorado School of Mines (CSM), and ALDN, coordinated well together.
- Collaboration appears to be appropriate, but it is not perfectly clear which organizations contributed on each slide. It may help to list, on individual slides, organizations that made direct contributions to the results.

Question 4: Relevance/potential impact

This project was rated **3.4** for its relevance to/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.

- As in the past, the relevance of the project is strong because of the role catalysts play in overcoming the cost and durability barriers to fuel cell commercialization. This is enhanced by the fact that the project is working on a low-platinum-metal-group (low-PGM) catalyst, which has a considerably shorter road to commercialization than a PGM-free catalyst. The one valid basis for questioning the project relevance would be if the project had no intent of addressing high-current-density (HCD) performance. Developing a catalyst just for the sake of high mass activity could actually be irrelevant, especially given the efforts by developers not to have stacks ever operate at 0.9 V cell potentials (for the sake of durability). However, the project has clearly shown polarizations measured under hydrogen/air at higher current densities. Although desired performance has not yet been achieved, progress has been made toward higher power density, and the project is targeting higher power density.

- The project is relevant to DOE’s 2020 target of achieving 0.125 g/kW combined PGM content in both electrodes. The new approach of making high-performing catalysts using the ALD method to achieve catalysts with high mass activity and possibly durability is expected to make a great impact on DOE's overall mandate to commercialize FCEVs.
- Extended surfaces address many of the limitations associated with nanoparticulate-based materials, giving this project a high level of potential significance.
- This project represents a potentially effective approach to manufacturing low-loading electrocatalysts.
- New catalyst work is important. It is important to evaluate structural changes for potential significant improvements. However, the massive size and hollow nature of the wires is of concern for meeting metal area and loading targets.
- The project is directly relevant to the DOE catalyst targets. However, it is unclear whether the performance, electrocatalyst durability, and activity challenges in MEAs are resolvable over the remainder of the project term.
- Reducing PMG loading is critically important to the successful commercialization of PEM fuel cells. The potential for this conceptual approach to be successful has not been demonstrated.

Question 5: Proposed future work

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

- Key issues are addressed, and the team is there to do it.
- On slide 19, the team has identified and listed the remaining challenges in the project and proposed them as future work. The “post-processing optimization” and “minimization of mass activity/[electrochemical surface area] of the catalyst” are two of the most important actions, which the team has acknowledged. The team’s planned future work is aligned with the project’s remaining challenges. The team could have included some durability cycle studies (e.g., load/humidity cycling and start/stop cycling) to get vital information about the ALD-made catalyst durability under automotive operational condition.
- The proposed future work is good. More detail is needed in terms of the electrode optimization to decrease transport losses. A strategy to move beyond carbon additives for improved HCD performance would be ideal.
- Approaches to performance issues are clearly defined; however, mitigation of durability issues could be improved.
- Optimization of ALD batches is discussed in the future work, but the priority for optimization is missing. It is unclear if catalyst durability, high-current performance, or mass activity (or a balance of these) is preferred for optimization. Robustness is missing in the future work. Perhaps even more important than scaling up is understanding how the catalyst responds to cold temperature, hot temperature, and load transients. DOE-prescribed testing should be done. It is good that the future work addresses durability studies and examining sources of voltage loss. However, these are fairly wide areas, and plans should be described in greater specificity.
- The proposed future work appears to align logically with the current project status and what is needed to bring the technology to the next stage. However, the primary focus should be on determining whether the catalyst can be successfully integrated into MEAs with high activity and performance and whether the catalyst is durable toward potential cycling, rather than determining whether the catalyst can be scaled up to the next stage for additional ALD process optimization.
- Future work needs to focus more on the verification of Ni stability and on the control of process variations.

Project strengths:

- This is a rare catalyst project with a well-established means of scaling up the material. The project has a concept that lends itself to high specific activity and mass activity, and has been able to execute both using ALD. The ALD process should be repeatable, and the results so far show that it is. This has been shown without wasting taxpayer money on over-engineering a system to accomplish prescribed repeatability targets. The project has taken care to remove excess Ni while still retaining the Ni needed for catalytic activity.

- The approach of using NW as a support system is good and has high potential to achieve durability targets. Moving to Co NW to minimize Ni content in the electrode, and hence minimizing the chance of Ni poisoning, is a good approach. The team is composed of highly qualified subject matter experts, which gives them a higher chance of the project's having a successful completion.
- This project has clearly demonstrated synthesis and scale-up of ALD-derived low-Pt loading electrocatalysts for oxygen reduction reaction. The project has done an excellent job characterizing properties and improving performance and has clearly identified remaining barriers.
- The unique catalyst structure, which has demonstrated mass activity in RDEs, exceeds the DOE targets by multiple factors.
- This project group is very experienced with working in this field, and they have chosen partners that have proven themselves capable of successfully completing this project.
- Project strengths include ALD scale-up and Pt/Ni compositional control.
- The novel structure catalyst allows unique vision into solving electrode issues.

Project weaknesses:

- MEA performance and durability are the clear areas of focus for the remainder of the project. A pathway for improved HCD performance is demonstrated, but approaches to improved durability are less clear.
- The project still needs to make greater progress in three areas: durability (to lower voltage window cycling), understanding (specifically of voltage losses at HCD), and testing (for robustness to various temperatures). Power density needs to increase substantially to become attractive to the catalyst and MEA suppliers that would develop the technology further. The perspective of a catalyst-coated membrane or MEA supplier would help to accelerate electrode design.
- Durability would be expected to be higher for an extended material. The use of carbon negates some of the advantages of using an extended-surface material; carbon corrosion and material agglomeration issues still remain.
- Catalyst activity and performance in MEAs are highly suppressed relative to RDEs. Catalyst–electrocatalyst cyclic durability is not sufficient. Catalyst characterization is limited after fuel cell testing and durability ASTs.
- The team has no plan to do durability cycle studies (load/humidity, start/stop), which could give them better information about catalyst stability under automotive operational conditions.
- This project needs to develop the process and procedures necessary to verify that Ni will not leach out of the catalyst layer over time, for all operating conditions that are anticipated.
- Catalyst size and the high-transition-metal content are weaknesses.

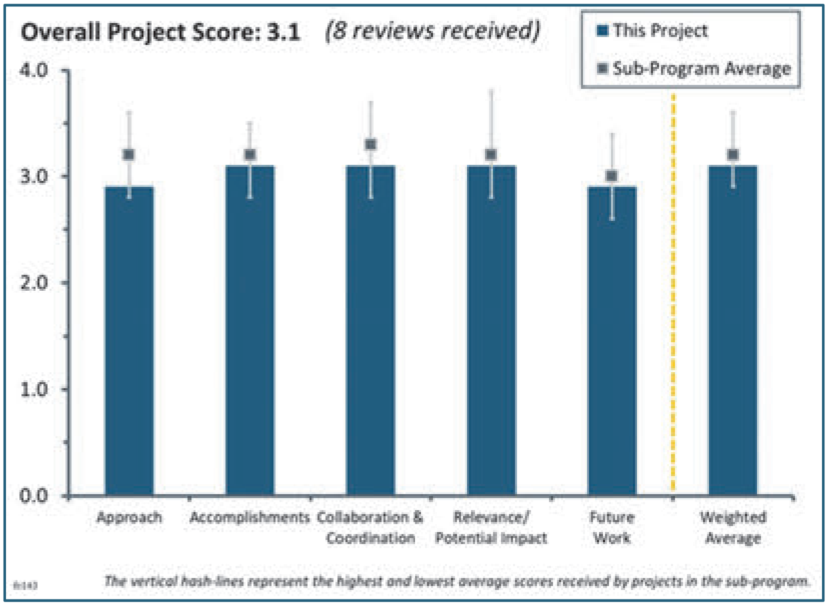
Recommendations for additions/deletions to project scope:

- Since mass activity measurements at 0.9 V are subject to variability, the intra-batch and inter-batch repeatability metrics might be more meaningful at HCD. Addition of a catalyst-coated membrane or MEA supplier might help to accelerate electrode design. It may be useful for the project to report whether there have been any problems that have arisen since using standard conditioning protocols.
- The project should propose alternative strategies beyond carbon to improve mass transport and HCD performance.
- Depending on the available time and funding, the addition of load cycling, humidity cycling, and start/stop cycling are suggested.
- Additional scale-up work and process optimization with the ALD partner should be halted until fundamental catalyst activity, performance, and durability concerns in MEAs are addressed. Significant additional focus should be placed on the catalyst cyclic durability assessment and the characterization of related materials. Integration into high-performance MEAs is also necessary to assess whether the achievement of rated power targets is feasible with the class of catalysts.
- If it is not already in the upcoming statement of work, the inclusion of image wires after metal AST is recommended, as is the confirmation of structural integrity.

Project #FC-143: Highly Active, Durable, and Ultralow-Platinum-Group-Metal Nanostructured Thin-Film Oxygen Reduction Reaction Catalysts and Supports

Andrew Steinbach; 3M

Brief Summary of Project:



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

This project is developing thin-film oxygen reduction reaction electrocatalysts on nanostructured thin-film (NSTF) supports developed by 3M. The aim is to exceed all U.S. Department of Energy (DOE) 2020 cost, performance, and durability targets through developing two different NSTF-based structures, nanoporous thin-film and ultrathin-film (UTF) catalysts. The electrocatalysts will be compatible with scalable, low-cost fabrication processes. The project will integrate the catalysts into advanced electrodes and membrane electrode assemblies (MEAs) that address traditional NSTF challenges, which include operational robustness, contaminant sensitivity, and break-in conditioning.

Question 1: Approach to performing the work

This project was rated **2.9** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The approach involves developing the ultrathin-film NSTF concept, with a particular focus on maintaining activity and durability, with very low-platinum-group-metal (PGM) loading. This approach is essentially an extension of what 3M has been doing for many years, but it has become more important since the recent demonstration that NSTF can be incorporated into dispersed catalyst layers.
- The down-select to the UTF approach made sense and seemed to help in evaluating other parameters such as Pt content and underlayers. The upcoming activity milestones are based on PGM content. There may be value in expanding the investigation of non-PGM sublayers.
- Progress toward the milestones is good. Even while the overall approach may not be viable, contributions to the understanding of catalysts and electrodes are good.
- 3M has been working on Pt and Pt-alloy catalysts deposited on NSTF supports for a long time, and it looks like the team still has issues to solve in terms of meeting the mass activity durability targets. 3M is continuing the approach in which Pt-based catalysts are deposited on NSTF supports (with various metallic underlayers) to achieve the DOE 2020 targets. The research is well supported through density functional theory (DFT) calculations and Monte Carlo simulation studies done by university partners.
- The approach continues to be primarily focused on developing more active NSTF-based catalysts, which is good, but it does not address the primary barrier to the success of NSTF in polymer electrolyte membrane fuel cells (PEMFCs), which is operational robustness.
- The project team’s approach is to develop radically different, catalyst layer physical structures, mostly on the micron-size level, as shown by the whisker structure on slide 4. This structure is vastly different from the structures made using conventional Pt/C catalyst materials; thus, the modeling should focus on the mechanisms/limitations of the transport properties of the whisker structures in fuel cell operation, rather than on the catalyst activity. It appears as if Johns Hopkins is doing this, but no data/modeling results were reported.

- The approach addresses fuel cell cost and durability barriers. The approach is focused on reaching activity and performance at high-power targets. Barriers specific to the thin electrode structures and NSTF-type catalysts, such as robustness and long conditioning times, are not addressed in this project. The DFT modeling has helped guide the experimental effort. The project goals indicate that the active area will be increased by integrating catalysts with higher-area supports. Efforts to integrate catalysts with higher-surface-area perylene-red supports (i.e., through higher whisker density or longer whiskers, etc.) are not apparent. Using Ir as an underlayer increases reliance on scarce resources.
- The project is aimed at mass activity, which is more related to catalyst activity. However, one of the most critical barriers of this type of non-ionomer catalyst layer is operational robustness, particularly hydration sensitivity. Any attribute of this barrier was not addressed in the project, and neither was any approach discussed. The requirement of long-time MEA conditioning is also a significant problem.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- 3M has been admirably thorough and diligent in investigating a huge range of different material additives to enhance the activity and durability of the PtNi UTF catalyst. Extensive work on Ir underlayers has helped to determine mechanisms by which UTF can be stabilized, though replacement of Ir with a non-precious material is needed for applications. So far, attempts to replace the functionality provided by Ir using alternatives such as Ta have been only partly successful. Much of the work has been performed using Pt NSTF (not alloys). Limited work with PtNi alloys suggests that the alloy composition will have to be re-optimized for use with the new metal underlayers. Results this year did not approach the high goals set for mass activity.
- The project has produced a good number of data with respect to catalyst preparation, characterization, and performance evaluation. 3M's UTF 31Pt/26Ir catalyst, especially, showed durability under catalyst and support accelerated stress test protocols. However, it appears that the mass activity of this catalyst is much lower than the 2017 result shown for the UTF Ir/PtNi catalyst. It would be good to see the Pt and Pt-alloy dissolution data, since the research is producing ultrathin catalyst layers.
- Milestones are being achieved, and several materials are being made; the down-selects seem behind, but some interesting materials are being developed. Some of the stability analysis should be better supported in terms of post-testing analysis—fuel cell effluent analysis and decomposition rate would be helpful.
- As usual, the amount of work presented and apparent progress are impressive. However, there are minimal results with respect to operational robustness, which should be occurring as well—especially with the addition of the FC-155 project.
- The mass activity of the effect of Cr is good: 0.57 A/mgPGM. The Ir underlay was interesting, and the Pt base-mass activity was significantly improved. However, it is not good that it is PGM-based.
- The project has made progress toward increasing durability of UTF catalysts. 3M has met the DOE target for a high-power performance of 0.125 gPGM/kW, with an Ir underlayer system. 3M has not yet been able to use the same catalyst to achieve all the activity, high-power performance, and durability targets. Mass activity of the durable systems has been lower than predicted, based on modeling. Mass activity is far from the project target of 0.80 A/mgPGM.
- Although the 0.44 A/mg PGM milestone can be avoided in the go/no-go decision, it currently seems unclear how it would be met. Reducing the Ir content appears critical but has been commented on in the "Remaining Challenges and Barriers" slide. The inclusion of durability data in the "Technical Backup" slides is appreciated. While the Pt/Ir data show promising durability, there is significant loss for the Pt/Ta materials. If the Ir underlayer cannot be reduced, the use of a non-PGM underlayer to improve PGM-based performance may come at the expense of durability.
- The accomplishments should have shown more fuel cell data; only one polarization curve, with a very low open circuit voltage (OCV) of 0.85 V and two-minute hold time per data point, was shown. Also, the membrane type was not shown, and low OCV is indicative of ultrathin membranes, which could have lifetime/fuel utilization issues.

Question 3: Collaboration and coordination

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

- The project has excellent collaboration with two universities to perform modeling studies and two national laboratories to perform characterization studies. In the second year, the project has produced significant modeling data.
- 3M is effectively collaborating with the partners. There is a good collaboration between the modeling effort and the experimental effort.
- It is good to leverage academia (i.e., universities) and national laboratories, in addition to the industry principal investigator.
- This project is excellent with project partners. The contributions of the partners are clear, as is the significance of these contributions. However, it is not very evident if there was good collaboration with a related 3M project (FC-155).
- The collaboration with Argonne National Laboratory and Oak Ridge National Laboratory is helpful for utilizing advanced characterization capabilities. The collaborations with Purdue and Johns Hopkins University appear helpful to improving understanding of the underlying factors that determine performance and durability, although, given the high experimental throughput in this project, it seems that direct experimental measurements could provide most of the critical data needed to build this understanding.
- The collaborator contributions were clear. The need for modeling may be limited with the increasing focus on cell performance, but it was appropriate, particularly with the earlier emphasis on simulation and a combinatorial approach.
- Collaboration is minimal but well executed.
- There were only university and national laboratory partners; modeling results from partners were limited to catalytic activity modeling, not transport modeling, which this project needs. This project would benefit from an original equipment manufacturer (OEM) partner to demonstrate MEAs in an independent laboratory.

Question 4: Relevance/potential impact

This project was rated **3.1** for its relevance to/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.

- The development of improved PGM-based catalysts is highly relevant and should continue to be a top priority of the Hydrogen and Fuel Cells Program (the Program). While NSTF has historically been of limited relevance owing to concerns associated with conditioning and robustness, recent progress on dispersed NSTF catalysts has addressed this issue.
- The research is highly relevant to the technical targets from the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan. The PtIr UTF catalyst has already met the technical targets for electrocatalyst and catalyst support durability metrics and exceeded the DOE 2020 target for PGM content.
- The project is relevant to the FCTO and addresses key barriers for fuel cells. The project advances progress toward meeting the Fuel Cell R&D sub-program’s targets and goals for cost, PGM loading, and durability. For commercial impact, break-in time must be reduced.
- If this is a catalyst project, then impact is routine, similar to other catalyst alloy projects. The potential of this project is the catalyst-layer structure and mass transport behavior, which has the potential to be tailored and controlled rather than having a fixed and arbitrary structure like conventional Pt/C has.
- The project addresses catalyst activity, cost, and durability. The project clearly supports and advances the goals and objectives of the Program.
- Besides good technical progress of NSTF, a critical problem is the robustness of this non-ionomer catalyst layer and sensitivity toward hydration of the catalyst layer. The project does not address this problem and does not set any attribute related to this operational robustness.
- NSTF catalysts can potentially have a major impact on PEFCs. However, the primary barrier for NSTF in PEMFCs is operational robustness. This project does not appear to address that issue significantly.

- The materials science component of the project is good, but overall, the underlying concept may not be implementable.

Question 5: Proposed future work

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

- It is good to explore the mechanism of effective integration with Ir or Ta underlayers. This has the potential to improve the catalyst performance if the PGM amount in the underlayers is properly controlled.
- Much of the “Remaining Challenges and Barriers” slide addresses the underlayers (Ir reduction or non-PGM) and performance. The “Key Future Work” slide is appropriate and follows logically.
- Future work is clearly planned and defined.
- The proposed future work mitigates risk by looking at methods to reduce PGM loading by replacing Ir with PGM-free underlayers and by using higher specific activity alloys to deposit on Ir underlayers. If 3M can replace Ir with a PGM-free underlayer and get similar performance from the Pt, the project can achieve its targets of 0.8 A/mg PGM, with <20% loss and MEA PGM content of <0.10 g/kW apparent. The proposed future work does not address known weaknesses of long break-in time and poor robustness/low-temperature operation of thin-film catalysts.
- The project includes a solid future work plan but is missing computational work on underlayers. High-current-density work would be good, as well as degradation product analysis.
- The proposed future work is highly ambitious owing to insufficient time, since the project will end in March 2019.
- The proposed future work is more of the same, but it should include more durability and performance stability data.
- The proposed future work does not address operational robustness in a significant manner.

Project strengths:

- The project has the advantage of more than ten years of work on NSTF-based catalysts, which makes it possible to better understand the system and perform necessary surface modifications to achieve DOE technical targets. The project has already met most of the DOE 2020 targets for electrocatalyst and catalyst support.
- The project focus is in the right places. A large number of material combinations and parameters have been evaluated, and there is a clear understanding of the remaining project challenges. Further development of NSTF-based catalysts provides value and aligns with FCTO priorities.
- The 3M team has excellent testing capabilities and has been able to test a large range of candidate materials and structures, enabling significant learning and development of promising catalysts.
- The project’s strength lies in the quality of the experiment, as well as the material fabrication process of physical-vapor-deposition-based catalyst layers.
- This project has excellent materials science development, electrode testing, and throughput.
- The strength of this project is related to its continued improvements on NSTF catalysts, with respect to both performance and durability.
- This project has potential with the ability to tailor the structure of catalyst layers.
- The high durability of the NSTF systems is a strength.

Project weaknesses:

- The structures are going on 20 years of demonstrations—better mass transport understanding should be key for future work.
- The approach relies excessively on Edisonian testing. For instance, while several surface modifier species have been investigated, there does not seem to be an explanation for how they were selected, other than trial and error. A more targeted research and development plan based on clear fundamental principles could be helpful.

- Project weaknesses primarily center around performance and whether there is a clear path forward for improvement. Since a significant number of parameters have been evaluated, it may not be possible to meet higher targets (0.44 A/mg PGM) with the PtIr and PtTa systems being evaluated.
- There is minimal focus on NSTF catalyst layer development and (not surprisingly) little evidence of significant improvements in operation robustness.
- High current density and degradation mechanisms are not demonstrated, and cost is a factor.
- The project does not describe the scalability of the UTF catalyst. The durability of the UTF catalyst in short stacks may be an issue.
- The project avoided discussing one of the most critical technical issues of this NSTF technology.
- The long conditioning times required for these systems is a weakness.

Recommendations for additions/deletions to project scope:

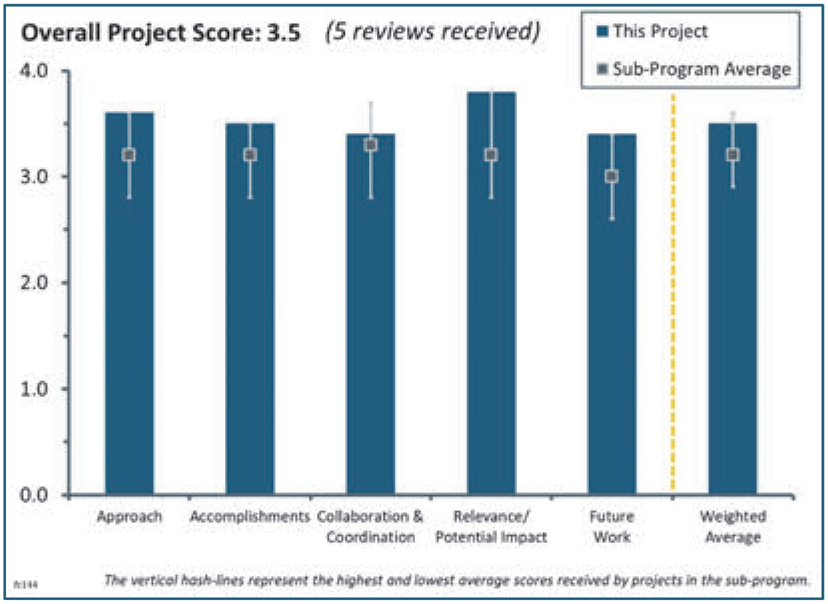
- There may be value in expanding the examination of underlayers beyond the Ir and Ta presented. There may not be a need to continue model development, with the increased emphasis on cell performance and with the gap between experimental activities and the model prediction.
- Adding more modeling work on the transport mechanisms in the novel structures is recommended. More data on the stability of the fuel cell performance as operating conditions change (i.e., drive cycles) should be added.
- There should be more emphasis on addressing operational robustness so 3M can sell NSTF MEAs to PEMFC developers, not electrolyzer OEMs.
- Recommendations include (1) analysis of fuel cell effluent for degradation products to understand stability of composite metals and (2) theory analysis of future conductive underlayers.
- The project should focus on developing ionomer-free catalyst layers utilizing UTF catalysts.
- It is highly recommended that the project be redirected toward operational robustness of NSTF.
- Work to reduce conditioning times would be beneficial.

Project #FC-144: Highly Accessible Catalysts for Durable High-Power Performance

Anusorn Kongkanand; General Motors

Brief Summary of Project:

This project aims to reduce overall stack cost by improving high-current-density performance in hydrogen–air fuel cells that meet U.S. Department of Energy (DOE) heat rejection and Pt-loading targets. Investigators will maintain high kinetic mass activities and mitigate catalyst degradation using supports with more corrosion resistance than the current high-surface-area carbon (HSAC). The project takes a four-pronged approach: (1) improve oxygen transport with new carbon support, (2) reduce electrolyte–Pt interaction, (3) enhance dispersion and stability of Pt-Co particles, and (4) improve understanding and control of leached Co^{2+}.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project is undertaking very important work needed to ascertain a fundamental understanding of low catalyst loading. The project follows an excellent approach. The team's iteration of characterizing and then reiterating materials development is very appropriate. The project employs excellent and very appropriate characterizations and uses outside team members on the characterization side well.
- The approach is sharply focused on achieving DOE targets in cost, durability, and performance. These multiple targets are addressed by focusing a research effort on both low- and high-current-density performance via intelligent selection of catalyst, support, and integrating modeling in the optimization process.
- The project follows an effective approach to understanding opportunities with a number of promising concepts, including the accessible carbon supports, the ionomer and ionic liquid interface approach, ordered intermetallic alloys, and the effects of the cations. For the accessible porous carbons, the approach is supported via theory, imaging, comparison to a number of structures, measurement of key parameters, and correlations with respect to local oxygen proton properties. It was not clear whether the project team has modeled the expected optimum. Understanding the proton resistance versus oxygen resistance is very important to drive further development. Rather than maintaining volumetric ratios of carbon to ionomer, the project team should control the surface-area-to-ionomer ratio to maintain the assumed similar ionomer thickness levels.
- This project is addressing a critical issue of hydrogen contaminant detectors (HCDs) with a low-platinum-group-metal (PGM) catalyst. This project has a very good collaboration scheme among many partners.
- Some aspects of the approach appear very likely to help overcome barriers, such as the use of accessible pores and ordered intermetallic alloys. Much of the work has been devoted to these parts of the project. Some aspects of the approach, however, do not appear likely to help overcome barriers. The use of ionic liquids was premised on the need to have ion-conducting species near platinum that do not confine themselves on the platinum (e.g., ionomer). However, through the two-year history of the project, ionic

liquids have not delivered promising results. In situ visualization of cobalt and cerium cations has not yet provided substantial results. The slides provided still leave the possible contribution of this work uncertain. Greater knowledge of the model would be needed to understand what the impact of this work would be.

Question 2: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The concept of accessible porous carbon was well established in the 2017 DOE Hydrogen and Fuel Cells Program Annual Merit Review. The modified HSACs have been used to show that pore volume, in a particular nanoscale regime, results in enhanced oxygen transport as well as enhanced proton transport. High-current-density results for PtCo, supported on accessible porous carbons, show the effectiveness of past efforts. Ordered PtCo/KB clearly shows an improvement in lowering mass activity and electrochemical surface area losses during the electrocatalyst cycling. Results showing the reduced proton transport loss at high relative humidity, as well as for carbons that anchor platinum on the exterior of a primary carbon particle, are very nice to see, but they are familiar trends from the year before. Robustness was very well shown with polarization results for low temperature, as well as for low outlet oxygen concentration.
- Excellent progress has been made toward understanding the mechanisms of transport losses at high current densities and toward design of a durable catalyst and support. Most of DOE's targets are met or have been closely approached with a PtCo catalyst supported on the new durable HSAC mesoporous support.
- The project team is making more progress than would have seemed possible. Very strong momentum has been observed on both transport and durability, in which the team is surpassing targets.
- Task 1 is completed. Different carbon supports are also being tried out. In situ synchrotron X-ray diffraction (XRD) and the scanning transmission electron microscope (STEM) were good tools for optimizing the Pt_3Co. It was good to see evaluations of various equivalent-weight ionomers and also ionic liquid integration in the catalyst layer (CL). If the long-term evaluation of the ionic liquid is not in the scope of the project, then resources and time should not be invested in it. However, looking at promising results with in CL, it would be worthwhile to see the durability of the ionic liquid, which is something that DOE and the principal investigator (PI) can discuss.
- The project team is finding some observed correlations between key parameters, such as oxygen reduction reaction (ORR) activity versus mesopore volume. Good improvements were observed in transport and activity by the creation of appropriate pore geometry. However, there appears to be a tradeoff in durability that will be important to address. The project team found increased platinum utilization through the use of ionic liquid and a higher performance. It is unfortunate that the project does not have data from test periods longer than one week, as it will be important to understand the ionic liquid's stability.

Question 3: Collaboration and coordination

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

- General Motors remains the driving force behind the project, with major contributions from Cornell University and the National Renewable Energy Laboratory (NREL). Cornell University appears to provide considerable help with PtCo stabilization, compositional analysis, and imaging. NREL provides considerable help with defining loss terms from fuel cell measurements. It does not appear that collaborations with 3M Company, Drexel University, and Carnegie Mellon University are as substantial as those from Cornell and NREL, which might be by design. However, the project could benefit from greater inputs from Drexel University and 3M Company if ionic liquids and perfluorinated imid acid ionomers can provide polarization benefits. The addition of these components to a CL is not likely to be trivial. Carnegie Mellon University appears to contribute three-dimensional imaging and modeling, most of which agrees with conclusions already drawn from other parts of the work.
- The project has some of the best collaborations that the reviewer has seen, in that each team member has a direct role and, more importantly, it relates directly to the project. Now that the project has shown the

importance of pore structure, it would be good to see the team working with someone who is more of an expert at controlling this going forward.

- Significant collaboration exists with a number of groups, including other industry representatives, national laboratories, and academics.
- There is excellent coordination between funded and non-funded partners. It is very clear who is doing what.
- This is a very well-coordinated effort between the team members.

Question 4: Relevance/potential impact

This project was rated **3.8** for its relevance to/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.

- The relevance of a catalyst project that focuses on improving high-current-density performance, especially over accelerated stress cycling, is self-evident. Power density and durability are well addressed in the Fuel Cell R&D sub-program targets. Better high-current performance can reduce the active area of the stack, which can have an impact on the overall cost of the stack. Using an ordered PtCo intermetallic to address durability is highly relevant toward enabling the use of high-activity materials.
- The project clearly aligns very well with DOE’s research and development and the Fuel Cell Technologies Office’s Hydrogen and Fuel Cells Program’s 2020 goals. Improving HCD performance of the low-PGM catalyst is very important, and this project is investigating and modeling this with an optimized catalyst and CL.
- The project directly addresses and has made great progress to both understanding and solving the problems of transport losses at very low loadings and catalyst stability. This would make the project an unqualified success.
- The work is highly relevant and addressing a key technical challenge that is impeding progress toward lower catalyst loading. The project is ultimately achieving DOE targets in a manufactureable design.
- The project is very well aligned with the DOE goals and has potential for significant impact on technology development.

Question 5: Proposed future work

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

- The project’s proposed future work is a logical continuation of a previous effort. It combines accomplishments from the previous phase of the project in terms of the catalyst, support, and CL design to meet DOE’s durability and low- and high-density performance targets.
- The project’s future work is well planned and relevant. It will be important to optimize the catalyst for both activity and durability. It would also be good to see a slightly longer test on ionic liquid.
- The project’s future work is appropriate, and it is winding down, which is a shame. As such, the project team is selecting final catalysts for membrane electrode assembly (MEA) delivery to DOE. It will be very interesting to understand the ionic liquid work better—especially its durability and retention.
- Models are mentioned, but details on how the models can be used and what benefit the models will create for the greater community are difficult to derive. Future work is focused on durability and high-current performance, which is appropriate. Nothing explicitly says that the ordered PtCo will be combined with accessible porous carbon developed earlier in the project, but presumably, that will be the case. The question-and-answer session revealed that durability testing with ionic liquid is outside the scope of the project, which calls into question why ionic liquid work should continue.
- If the ionic-liquid-integrated MEA will not be tested for durability, then not much effort should be put into it. The Fuel Cell Performance and Durability Consortium is showing very high ORR activities (~1 A/mgPt) in MEAs for commercial catalysts (e.g., Umicore) using more conditioning. This team should look into this approach and also investigate whether increased ORR activities after more conditioning has any effect on HCDs.

Project strengths:

- The project lead is an automotive original equipment manufacturer that has perspective on what needs to be done to commercialize fuel cell systems. The project team has developed a concept (accessible porous carbons) to address oxygen transport and proton transport losses at high current density, which can bring down the active area and cost of a stack. The project team has developed a material concept for durability, namely the ordered intermetallic PtCo. The project team has access to imaging, modeling, and tomography resources for a deeper understanding of catalyst phenomena.
- There is a clear focus on key technical challenges. There are strong collaborations incorporating the expertise of a number of groups. There is strong support of characterization and measurement on the experimental work.
- The project has a very strong team and PI who leads the project in a timely and efficient manner. The project combines the best expertise in synthesis, modeling, and evaluation of materials and fuel cells.
- The project has a strong team and collaboration, led by General Motors. The project team has undertaken balanced efforts on catalyst development and CL optimization.
- The project has great technical momentum with excellent teaming and characterization. The project follows a logical flow and performs relevant tests to prove or disprove this logic.

Project weaknesses:

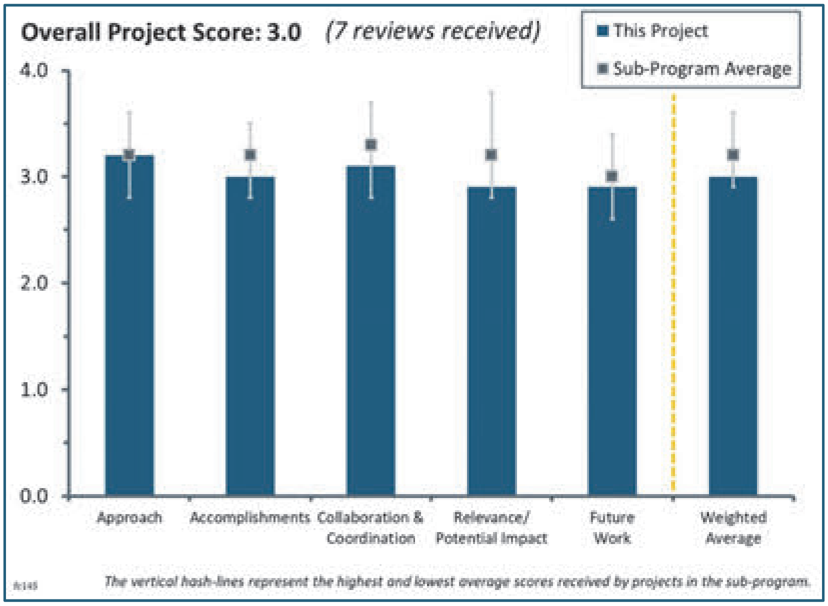
- There is only one catalyst candidate. Although many carbons supports are investigated, more catalyst candidates could have been better.
- The project team should benchmark against new commercial catalysts, which are showing very high mass activity in MEAs.
- Modeling appears to serve as a confirmation of what is already known. It is not apparent that the modeling is critical to the project. Ionic liquid and novel ionomer efforts do not appear to be “mainstream” to the rest of the effort. The project would be just as valuable without these work streams.
- The project team could have planned better for its successes. After showing the importance of pore structure, the project could have a better plan to control it. Similarly, the ionic liquid task has shown promise, somewhat to the project team’s surprise, but the team seems unprepared to do the next obvious steps: discovering whether it is durable, both chemically and physically (i.e., whether it “stays in there”).

Recommendations for additions/deletions to project scope:

- It is a well-thought-out project. No changes to the project scope are recommended.
- The project team should focus on the durability of ionic liquid in accelerated stress testing or remove ionic liquid work entirely. If modeling serves only as a confirmation of what is already understood, then the reduction of modeling efforts should be considered. Reporting should clarify the benefits expected from modeling cation transport.
- Obviously, the project team should follow up on the ionic liquid work. Also, it would be good to see some further work/investigation on the thesis that transport is taking place in condensed pores. This is very important to the fundamental understanding.
- The project team should work to increase the understanding of ionic liquid stability and durability.
- If ionic liquid in the CL is showing improved ORR, then it is worthwhile to investigate durability.

Project #FC-145: Corrosion-Resistant Non-Carbon Electrocatalyst Supports for Proton Exchange Fuel Cells

Vijay Ramani; Washington University



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

Brief Summary of Project:

Carbon’s high electrical conductivity and low cost make it an excellent electrocatalyst support, but corrosion leads to kinetic, ohmic, and mass transport losses. This project is synthesizing doped non-platinum-group-metal (PGM) metal oxides as non-carbon alternatives. Along with being corrosion-resistant, the project supports would have high surface area, exhibit strong metal–support interaction with Pt, and demonstrate high electrocatalyst performance.

Question 1: Approach to performing the work

This project was rated **3.2** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The approach addresses a critical barrier of durability and cost by attempting to provide a materials-based solution to the catalyst support corrosion experienced during fuel starvation and startup/shutdown conditions. The project is sharply focused on improving support durability. The project has been well designed and has demonstrated feasibility of the proposed supports. The investigation of these materials as anode supports, as well as cathode supports, would be beneficial.
- This project is looking at a fundamentally different approach to the support that could yield interesting results. With such a different approach, more fundamental modeling of the effects of the unique support properties on electrode performance may be useful.
- Pursuing non-carbon supports has long been a target to enable less system-based controls to mitigate carbon corrosion and start/stop concerns. The materials investigated and the synthesis methods explored merit further investigation.
- The approach is sound and effective.
- This project follows a clear approach, using doped metal oxides to replace carbon. The team is holding themselves to the general catalyst U.S. Department of Energy targets, which is a good thing; however, it would be good to see a conductivity target, as well as details about the team’s progress toward such a target. This is in a milestone that the project team says the project has met, but this has not been reported. It is clear that conductivity is a limiting factor on performance, so it should be a clear metric against which the team works.
- New materials have the potential to improve durability by overcoming carbon corrosion. It is unclear whether these materials support and help improve Pt mass activity and overall performance, compared to carbon supports. Density functional theory (DFT) modeling could help lower the matrix of materials to try and add information to help other projects.
- The presentation does not clearly state how the project will achieve the end-of-project mass activity target of 0.3 A/mg_{Pt}, considering its current status of 0.05 A/mg_{Pt}.

Question 2: Accomplishments and progress

This project was rated **3.0** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project has been able to develop high-surface-area doped TiO_2 supports with improved durability under start/stop cycling conditions compared to carbon supports. Rotating disk electrode (RDE) data indicates that the team can achieve oxygen reduction reaction (ORR) activity for Pt on doped TiO_2, which is higher than that for Pt/C. The project team has also developed Sb-doped tin oxide supports and performed durability tests with Pt/Sb–SnO_2 catalysts. The Sb-doped tin oxide supports showed much lower losses after start/stop cycling than Pt/C and higher performance after the cycling for Pt/Sb–SnO_2 than for Pt/C. The project team has been able to obtain electrochemical surface area values on the oxide supports comparable to those obtained for Pt/C. The initial performance of the Pt/Sb–SnO_2 was much lower than that for Pt/C. Activity for the Pt/Sb–SnO_2 should be reported. Performing a characterization of the pore structure would be beneficial. The beginning-of-life activity and performance at a high current density need to be improved. Humidity dependence and robustness need to be determined. The oxide supports may have more problems with flooding and startup at low temperatures. The strong metal support interaction offers the potential to increase durability during the catalyst degradation cycling protocol. Samples should be tested under the catalyst durability cycle to see whether the strong metal–support interaction (SMSI) has an impact on catalyst durability in the catalyst durability cycle.
- Great work is being done on demonstrating the durability and developing some of the understanding behind it. The team states that the supports can increase activity, but other than theory, there is not really much evidence toward that; other than RDE, an increase in activity does not seem to show in full cell testing.
- Both of the two down-selected materials show merit and meaningful improvements over the past year. In particular, the report on fuel cell performance and durability shows promise. However, the high resistances found in fuel cell tests and limited mass activity remain challenges with no clear path to overcoming.
- The team showed that a completely new non-carbon support could function in a polymer electrolyte membrane (PEM) fuel cell; this is a significant accomplishment. However, the MEA performance is not close to where it needs to be for this to be a useful support, although the team has made progress.
- Meaningful milestones and membrane electrode assembly (MEA) tests were accomplished, despite a delay.
- The ORR onset potential for Pt/Nb–TiO_2 and Pt/C seem to be identical. It is not clear why the mass activity is different, but neither is very close to meeting the DOE target of 0.44 A/mg_{PGM}. Other Pt/C catalysts have been shown to have much higher mass activities compared to the one shown here, but it is unclear why these mass activities are as low as they are. Of course, Pt/Co and Pt/Ni could surpass the mass activity targets. Pt/C is likely not an appropriate comparison for the mass activity target. Stability against the DOE/Fuel Cell Technical Team carbon corrosion accelerated stress test (AST) looks good. MEA durability looks good, although performance is lacking. The cause of the relatively low performance is unclear, but the Tafel region looks to have large losses. A voltage breakdown might be informative to separate additional kinetic losses versus additional iR losses versus a Pt/C baseline.
- Only one MEA test result for the startup/shutdown protocol is presented (on slide 14) for fiscal year (FY) 2018. The project team should perform more fuel cell testing.

Question 3: Collaboration and coordination

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

- The project collaboration is good for understanding the fundamental characteristics of supports and/or catalysts and for evaluating their fuel cell performance and durability. Both the objectives have been met with the collaboration involving a second academic institution (The University of New Mexico [UNM]) and an original equipment manufacturer (OEM) (Nissan Technical Center North America [NTCNA]), respectively.
- Collaboration between the partners appears to be going well. Collaboration with the Fuel Cell Consortium for Performance and Durability may be beneficial, especially concerning the optimization of the ionomer content, Pt–support ratio, and support structure/porosity to optimize performance.

- This project contains good collaboration with appropriate partners. One group is making supports, another the catalysts and fundamental characterization, and the OEM is doing the final testing characterization. It appears that Nissan is not sharing much data, and Nissan's work seems a bit opaque.
- UNM accomplished the DFT and some characterization, and Washington University (WU) completed the synthesis; it is unclear what entity did the RDE and MEA testing, including the 1.0–1.5 AST, but assuming it was Nissan, this seems to be a well-coordinated collaboration. At this point, it is hard to tell whether the DFT modeling is really being used in the synthesis activities.
- For a large project, this is a small team, although have most critical aspects seem to be covered. In particular, a ceramic company, or at least someone more familiar with the large-scale manufacture of support materials and the technoeconomics of support production, would be valuable.
- UNM and Nissan are providing complementary contributions. However, the project is missing capabilities with the modeling of electrode performance based on the catalyst properties.
- Collaboration outside WU and NTCNA is not clear; iterative interactions are also unclear.

Question 4: Relevance/potential impact

This project was rated **2.9** for its relevance to/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.

- Catalyst corrosion is a huge challenge, and this project is demonstrating a viable path to achieving high-potential stable supports and catalysts.
- The project is relevant. The potential impact will depend on the relative cost to implement these oxide supports versus the cost of current system mitigation strategies. It will also depend on whether the oxide SMSIs offer additional advantages in the catalyst degradation cycle (0.6V–0.95V), compared to carbon supports. The supports may be more relevant as anode supports than cathode supports.
- The project is fundamentally interesting and could potentially improve oxidation resistance of catalysts; however, it seems unlikely this catalyst will be useful for an automotive fuel cell because of the low performance. The impact of this project may ultimately be for higher-temperature fuel cells or electrolyzers.
- This project appears to be primarily addressing the durability issue with carbon corrosion. There is discussion about improving mass activity, but that does not seem to be much of a goal, and it is unclear what activities will lead to an improved mass activity. An increased mass activity does not appear to be a major focus of this project. Many of the state-of-the-art (SOA) numbers appear significantly off from what others consider to be the SOA. For example, the mass activity is listed at 0.07 A/mg_{PGM}, where PtCo, a relatively old material used in the Toyota Mirai, has a mass activity clearly upwards toward 0.4 A/mg_{PGM}, while other laboratory catalysts regularly show mass activities >0.44 A/mg_{PGM} (the DOE target). The end target for this project is only 0.3 A/mg_{PGM}, which, if attained, is still not even the current SOA. A similar discussion on PGM loading can be had. This project should be much more aggressive with its end targets. Improved catalysts that reduce the fuel PGM content is one of the critical areas in which this project can make a near-term impact; this potential impact includes higher activity and improved durability.
- Metal oxide supports are known to be stable under high potential cycling conditions, such as 1.0–1.5 V. However, the proposed mass activity target (i.e., the end-of-project value) is much lower (0.3 A/mg_{Pt}) than the DOE 2020 mass activity target of 0.44 A/mg_{PGM}. It is unclear from the presentation how the mass activity target will be achieved by the end of the project.
- The project does have relevance in terms of durability against carbon corrosion, but the team does not address other DOE targets. Durability against carbon corrosion is perhaps one of the least critical metrics in the DOE target tables because of the ability to mitigate through system control strategies.
- If successful, these supports might well be implemented. However, they seem far away from traditional supports, and carbon supports are continuing to make progress. Hence, it is doubtful that these supports will come close enough to carbon to make a difference.

Question 5: Proposed future work

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

- It is not clear that the team wants to go to higher Pt loadings on the support; because of the higher density of these supports compared to carbon, the current loadings are comparable to or higher than the volumetric loadings of Pt on carbon. The proposed future work addresses the key areas of increasing surface area of the support and MEA optimization.
- The proposed research is sufficient to overcome some of the technical barriers presented in slide 18.
- The project should concentrate on increasing the mass activity of the catalyst, which may have to include using an alloy such as PtCo. The DFT calculations should possibly guide the synthesis for higher mass activities; while conductivity is (and can be) an issue, the project needs higher mass activities.
- The future work appears to be focused on a continuation of the work performed to date. The proposed work is reasonable, but it does not suggest further improvements to some of the more critical barriers that are not specifically addressed in the project—namely, improvements to increased mass activity and rated power, as well as perhaps addressing flooding issues caused by the use of such a dense thin-film electrode.
- The project team needs to increase both the conductivity and the surface area of the supports. However, as the team pointed out, these are tradeoffs, and this will be difficult. Increasing the active area and translating RDE results to the full cell are good goals, but it is not certain that the team has a reasonable path toward this.
- Considering recent personnel changes, the role of UNM is unclear, considering recent personnel changes, but WU and NTCNA work is appropriate.
- The support may have properties that make it unable to achieve DOE targets in an MEA, such as sufficient conductivity, porosity, and hydrophobicity. The proposed future work may not address the shortcomings with regard to such properties.

Project strengths:

- The project has developed stable conducting oxide supports with good Brunauer–Emmett–Teller (BET) surface areas that enhance the stop/start durability.
- The project is pursuing a unique approach that could drastically improve support oxidation resistance. This approach could be useful for other types of fuel cells (particularly intermediate temperatures) and electrolyzers.
- This project’s strengths include collaboration with UNM for modeling and a sacrificial support method for making high-surface-area metal oxides, as well as Nissan for durability testing.
- This project has demonstrated superior durability performance to the carbon corrosion (1.0–1.5 V) potential cycling AST.
- This project has demonstrated two supports that have shown promise for increased corrosion resistance and have reasonable electrochemical properties.
- This is a good collaborative team with an appropriate approach. The work and results on durability are excellent.
- The project has a great and proven approach.

Project weaknesses:

- The team is plateauing on what the project can do with these supports. The supports are already too resistive, and it is necessary to increase porosity and surface area, but doing this will only hurt conductivity further. It is not certain that the team has a pathway to increase intrinsic conductivity.
- There is a lack of a ceramic/support synthesis company to better assess options for large-scale synthesis and commercialization. There is also a lack of an impact on a number of DOE targets, with a primary focus on carbon corrosion issues.
- The catalyst made in this project does not show competitive performance in terms of mass activity, and there seems to be little in the plans to increase the mass activity to where currently available catalysts are.
- Based on the results reported so far, this approach will probably not simultaneously achieve all of the DOE 2020 targets for automotive fuel cells.

- The cost and manufacturing analysis, as well as material compatibility for the new supports, should be considered.
- There was difficulty in achieving mass activities higher than the value reported in FY 2017.
- The resistivity is a little bit high.

Recommendations for additions/deletions to project scope:

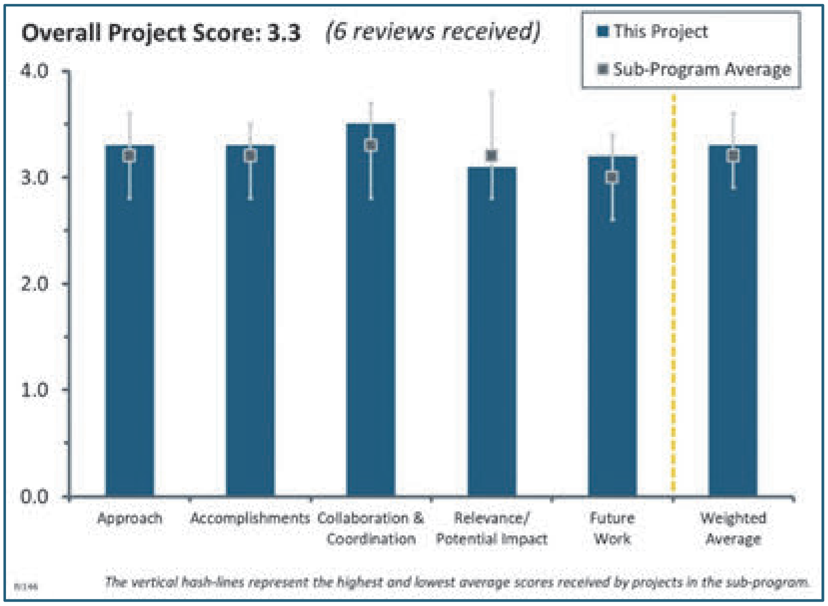
- The project team members need to understand the limitations that conductivity is placing upon performance. If the underlying support does not have that, the team can save themselves a good deal of time in adding the catalyst and making MEAs. In this regard, much of the future work includes the scale-up, manufacturing, and characterization of MEAs. If the underlying supports will not get the project where it needs to be, the team should put more focus on that future work.
- Electrode modeling could possibly be beneficial to this project. Exploring other applications should be considered because achieving the automotive targets for a PEM fuel cell does not seem realistic within the project timeframe.
- This project should concentrate more on improving mass activity; this could include the use of an alloy such as PtCo. Until mass activities are competitive, enhancing mass transport should not be a priority.
- Perhaps anode testing and validation should be substituted for the unclear UNM future contribution. Some technoeconomic analysis of the viability of these new catalysts should also be included.
- A focus on increasing mass activity to a relevant range, perhaps by investigating alloys, is recommended. A focus on electrode flooding issues is also recommended, and the concern over the relative humidity dependence on performance should be investigated.
- It is recommended that the project team add work to look at using these supports for the anode.
- The project should focus on more fuel cell testing.

Project #FC-146: Advanced Materials for Fully Integrated Membrane Electrode Assemblies in Anion-Exchange Membrane Fuel Cells

Yu Seung Kim; Los Alamos National Laboratory

Brief Summary of Project:

This project is developing advanced materials for fully integrated membrane electrode assemblies (MEAs) in anion-exchange membrane fuel cells (AEMFCs), enabling fuel cell cost reduction without sacrificing performance. The improved anion-exchange membrane (AEM) materials are based on highly conductive and stable hydrocarbon polymers. The project also aims to address challenges with integrating catalysts and AEMs into high-performance MEAs. The approach involves (1) preparing AEMs without aryl-ether linkages in the polymer backbone and (2) developing different ionomeric binders for anode and cathode.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The team has correctly identified the critical barriers regarding polymeric materials for alkaline fuel cells: polymer performance, stability, and durability in a fuel cell. The use of aryl-ether-free polyaromatic anion-exchange polymers is the correct approach to take. The ionomers developed in this project have been used as both the membrane and electrode binder in alkaline fuel cell MEAs. The project is well integrated with other AEM fuel cell efforts.
- This is a systematic approach to modifying polymer backbone and functional groups to reveal AEMs' weak points and systematically eliminate them.
- Critical barriers have been identified and are being addressed. The project is integrated with other relevant efforts on alkaline membranes and fuel cells. The project has previously identified cation groups that are more stable than the (hexyl) trimethyl ammonium cation being used in the current membranes. Degradation of this cationic group appears to be responsible for the observed losses in conductivity of about 50% in ex situ alkaline stability tests over roughly 2000 hours. It is not clear why the more stable cationic groups identified in earlier work (such as the resonance stabilized cations described in 2017) are not being utilized in the down-selected membranes. The hydrogen oxidation reaction (HOR) is sluggish in AEMFCs compared to polymer electrolyte membrane fuel cells (PEMFCs), and durable high-activity platinum-group-metal-free (PGM-free) HOR catalysts have not been developed, so the potential advantage of an AEMFC over a PEMFC has not materialized. A major weak link is the HOR catalyst, and this project has not addressed that barrier/weakness.
- The most critical barriers, such as membrane stability in an alkaline environment, AEMFC performance, and durability issues, have been addressed. However, more fundamental barriers for the application, such as the impact of carbonate/bicarbonate formation and its impact on membrane stability/properties and on performance and durability on a fuel cell level, have not been addressed.
- The approach to show membrane stability with ex situ aqueous experiments and steady-state H_2–O_2 tests is okay for initial screening but far from conclusive. Factors such as drier conditions, voltage cycling, and

humidity cycling must be considered. The approach of using model compounds to screen for ionomer adsorption on Pt-Ru seems reasonable, but the team needs to verify that density functional theory (DFT) results correlate with fuel cell performance. Also, the team should look at non-PGM catalysts for the adsorption studies. The approach of using diallyl phthalate (DAP) polymers is questionable. They are very brittle in polymer electrolyte membrane systems. It is not clear why AEM systems would be any better.

- The project's approach is okay, but the major motivation for AEMFCs is to use non-PGM catalysts; however, this project is doing very little in this area. It is understandable that a polymer chemist wants to focus on membrane development, not catalysts, but then it is questioned whether the project title should be "Advanced Materials for Fully Integrated MEAs in AEMFCs."

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Progress has been good and noteworthy. The project team has met or surpassed many/most of the DOE fourth quarter (Q4) 2017 metrics, including membrane area-specific resistance, AEMFC performance, and AEM durability. Materials have been screened and down-selected—an appropriate approach that has proven to be successful. Numerous MEA fuel cell polarization plots were shown during the Hydrogen and Fuel Cells Program Annual Merit Review (AMR) presentation, an indication that significant membrane/polymer progress has been made. The team has nicely addressed AMR comments from last year, including the investigation of non-PGM electrode catalysts. There is a good effort here by the team. The project end date is approaching, so the AMR presentation included numerous MEA performance plots.
- The project has made significant progress in the area of alkaline membrane durability and AEMFC performance. The project has exceeded AEMFC performance targets and is approaching durability targets. Work from this project has been instrumental in the increased understanding of AEM durability issues and catalyst alkaline–ionomer interactions. The work investigating the interactions of ionomer phenyl groups with the HOR catalysts, and the resulting development of skewed aromatic rings to limit phenyl adsorption, are major contributions to the field.
- As shown on slide 3, performance goals have been met or exceeded. Durability goals have nearly been met and are in progress.
- Very good progress has been made in terms of demonstrating high-power density. The down-selection process in finding promising candidates for stable membranes and suitable ionomers in the electrode led to a number of promising materials. The low PGM loading on the anode side is a very promising result. However, more results should be generated/shown regarding the properties and aging behavior of membranes and electrodes, such as changes in conductivity, membrane integrity/mechanics, and catalyst structure. The impact of ink preparation and the structure of the electrodes could be carved out more clearly.
- As far as AEMs are concerned, the beginning-of-life (BOL) performance and steady-state durability after 500 hours are on the right track. The mechanical durability and robustness at dry conditions cause concern. The high performance loss after 500 hours steady-state is very concerning, especially with no specific ideas provided to address the degradation. The accomplishment of identifying phenyl-group adsorption as a limiting factor is nice, but not surprising.
- There is good progress, especially with respect to studying degradation mechanisms. However, important aspects, such as air tolerance, continue to be ignored. It was stated that this concern has been addressed by having a back-up slide with an air polarization curve. However, the test was run with CO_2-free air. This is concerning since the major concern with air is CO_2.

Question 3: Collaboration and coordination

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

- Los Alamos National Laboratory (LANL), Sandia National Laboratories (SNL), Argonne National Laboratory (ANL), and Rensselaer Polytechnic Institute (RPI) form a complementary and complete team

on making functional groups, the polymer backbone, modeling, and the catalysis of alkaline electrolyte membranes. There was no redundancy, and the team was well coordinated, with a reasonable budget.
- Collaborations within the project are going well. The project appears to be coordinating with an unnamed industrial partner, and coordination with the National Renewable Energy Laboratory and others in the overall field of AEMFCs is apparent.
- The project team is strong. SNL and RPI provided ionomers. ANL provided low-loading catalysts. Non-funded partners such as Technion also provided analysis.
- All major laboratories, institutes, and universities in the field seem to collaborate. The transfer of materials and data seems effective.
- The contributions from project team members is clear, and there are many interactions with others.
- The project is a collaborative effort with LANL as the lead, with SNL, ANL, and RPI performing support roles. The roles of SNL and RPI are obvious (i.e., polymer synthesis), whereas the ANL tasks were not well defined/explained. There are numerous other non-funded partners on the project, as per slide 15 in the AMR presentation. Their level of effort and the importance of their contributions was not clearly explained during the presentation.

Question 4: Relevance/potential impact

This project was rated **3.1** for its relevance to/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.

- Over the years, AEMs were considered intrinsically unstable. Thanks in no small part to this project, the stability of alkaline membranes has been greatly improved and will continue to be improved through rational improvements. This will open the door to inspecting the value of AEMFCs based on measurements, not guess work. Although a long way remains to an AEMFC, there have been some very interesting uses of AEMs in fuel cells, in particular, the use of a fluorene unit to make high-power (1.5 W cm^2) AEMFCs; another surprise is a self-hydrating bipolar membrane fuel cell that uses a cation exchange membrane and an AEM (see the *Journal of Power Sources*, vol. 299 [2015], p. 273–279).
- There is a need to examine/develop durable alkaline fuel cells that produce high power without the use of precious metal catalyst electrodes. The project team has made excellent progress in developing a high-power alkaline fuel cell and is investigating new AEM polymers with improved chemical stability, which is important. The team is also modeling water transport in an operating MEA, an issue that needs such attention.
- Alkaline exchange membrane fuel cells have potential for reversible fuel cells, where pure oxygen that is generated during the electrolysis step can be utilized in the fuel cell mode and can potentially enable PGM-free oxygen evolution reaction/oxygen reduction reaction catalysis. The project area of alkaline exchange membrane fuel cells is not well aligned with the transportation focus of the Fuel Cell Technologies Office. AEMFCs have several issues, the largest one being operation with air and the conversion of the membrane to carbonates, which has a large impact on membrane conductivity and performance. Other issues include HOR performance (leading to use of PGM-based catalysts) and lower power densities than PEMFCs.
- The project and its findings help in understanding the fundamentals of AEMFCs. However, the general feasibility—whether AEMFCs can be operated under ambient conditions and can contribute to reduced fuel cell costs by making PGM catalysts obsolete—has not been addressed; therefore, the progress toward the overall DOE goal cannot be assessed.
- AEMFCs are an interesting low-technology-readiness-level technology, which could have a major impact. However, this project is primarily limited to polymer-development progress that is necessary but not sufficient.
- It is difficult to assess relevance without a targeted application. Assuming an automotive application, the relevance is fairly low, as the trajectory for system cost and power density does not match that of PEMFC systems, which will not require carbon dioxide scrubbing or a complex water management system.

Question 5: Proposed future work

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

- The future work outlined on slide 17 is all good: synthesis scale-up, non-PGM catalysts and reinforcing membranes, and further work to identify durability-limiting factors. In terms of durability, both the chemical instability of the polymer and the effects of CO_2 from the air on the anion (hydroxide or carbonate) type are the most important factors to address to make AEM fuel practical.
- Many remaining barriers are addressed, and it seems necessary to upscale the material synthesis. It would be helpful to focus also on catalysis, electrode preparation, and the analysis of the resulting electrodes.
- The proposed future work is mostly appropriate for the time remaining in the project; however, work with more stable cationic groups with a fluorene backbone would be good to add.
- The proposed future work is good since it claims the project will focus on durability and non-PGM catalysts.
- Future work will focus on synthesizing the down-selected AEM ionomer in larger quantities, completing MEA performance tests, and finishing up durability testing. There is a need to establish some kind of accelerated stress test (AST) for AEM durability to replace a constant current (or voltage) hold test.
- The top priority should be to identify the durability-limiting factor(s). The demonstrated 200 mV voltage loss in 500 hours of steady-state testing with platinum electrodes is far from acceptable. No scale-up should be done until it is known there is a semi-durable product. No indication of ideas or concepts to address the durability problem was presented.

Project strengths:

- The project addresses an important subject: the development and testing/evaluation of polymeric materials for the membrane and electrode binder in alkaline fuel cell MEAs. The project team has made considerable progress in meeting the project milestones and go/no-go decision points.
- One strength is the encouraging demonstrated BOL performance in oxygen- and carbon-dioxide-free air. This is a strong team, and there is interest from the fuel cell community in technology transfer. The fundamental approach to electrode ionomer selection is a strength.
- There is broad and good collaboration between all institutions involved. Good and promising materials and analytic capabilities are available.
- The strengths of this project are the innovations to improve stability and performance of fuel cells with anion-conducting polymers.
- This is a well-coordinated project that has done seminal work in the area of AEM durability.
- The strength of this project lies in the polymer chemistry.

Project weaknesses:

- The PI claims to have met a major AEM target (0.6 V at 0.6 A/cm^2), but this was *not* done at the required catalyst loading. In fact, the catalyst loading is >10x higher than the target, which is 0.1 mg PGM/cm^2 (p. 42 of the Multi-Year Research, Development, and Demonstration Plan). An 11,000-hour stability test has not been completed, since the conductivity was not stable during this period of time. Also, the time limit for AMR presentations should be better observed. There was insufficient time left for questions, and there are many questions when one makes big claims with materials that do not really meet the metrics.
- Membrane durability remains unproven at realistic, non-steady conditions. There is high voltage degradation, even with platinum electrodes and steady-state conditions, and there is no plan shown to address this weakness. Other weaknesses include a lack of adsorption studies with non-PGM electrodes and no ionomer durability.
- There were no obvious weaknesses in the project tasks and timeline. The team has yet to show good fuel cell performance with a non-PGM cathode catalyst. AEMFC durability continues to be an issue. There is no established method of assessing long-term durability in a short-term AST.
- AEMFC applicability to transportation applications is questionable because of problems with the carbonate/bicarbonate formation when operating on air.

- This project cannot contribute to answering the question of whether the fundamental problems in AEMFCs (e.g., CO_2, anode kinetics) can be overcome.

Recommendations for additions/deletions to project scope:

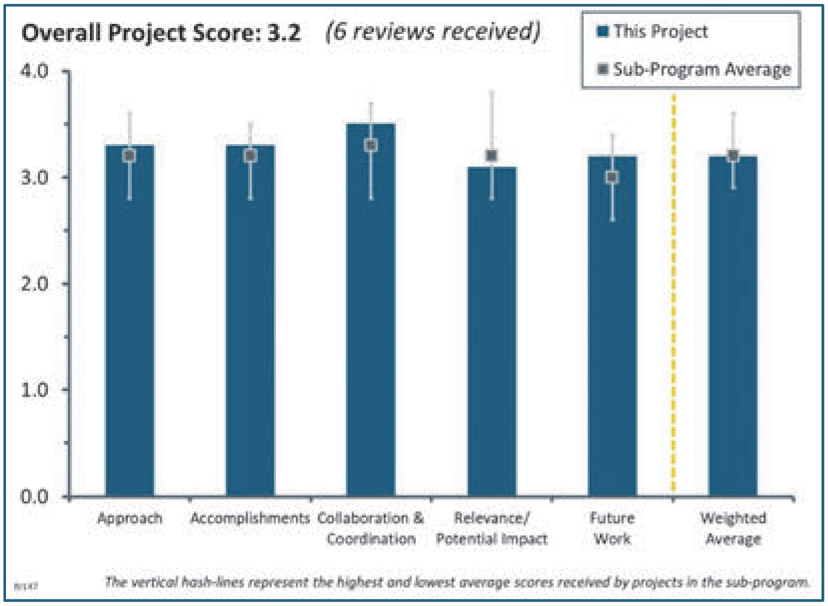
- It is recommended that the project continue to focus on MEA testing. Using a PGM-free cathode catalyst and setting specific performance targets for the membrane and binder are suggested. There may be a need to optimize on the conductivity/ion exchange capacity and thickness of the membrane in an AEMFC MEA. Right now, the PI is using a 40-µm-thick membrane. It would be interesting to see if a thinner membrane could be used (with reinforcement) for mechanical strength.
- The team should hold off on scale-up until durability issues are understood. The team should focus on the root cause of performance losses. The team should add to the project scope: membrane durability at dry and dynamic conditions (e.g., relative humidity, temperature, voltage cycles), membrane mechanical characterization (e.g., swelling, strength, stiffness), and DFT adsorption studies on non-PGM catalysts.
- Work with cations with resonance-enhanced stability and a fluorene backbone is recommended.
- It would be helpful if the preparation methods and the structure of the electrodes had an impact on the performance and durability.
- This work should be continued so that the team has the chance to address stability in more detail.
- Exaggerated claims should not be made. One should not claim to have met DOE milestones when that has not actually been done. The use of PGM catalysts, for now, is understandable. However, very high loadings should not be used.

Project #FC-147: Advanced Ionomers and Membrane Electrode Assemblies for Alkaline Membrane Fuel Cells

Bryan Pivovar; National Renewable Energy Laboratory

Brief Summary of Project:

Alkaline membrane fuel cells (AMFCs) offer promise for improved performance and decreased cost. This project aims to develop novel perfluoro (PF) anion-exchange membranes (AEMs) with improved properties and stability, employ high-performance PF-AEM materials in electrodes and as membranes in AMFCs, and apply models and diagnostics to AMFCs to determine and minimize losses (water management, electrocatalysis, and carbonate-related). Researchers will synthesize, characterize, and optimize AEMs and fuel cells for performance and durability.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- This project takes on the difficulty of AEMs with the added difficulty of perfluorocarbon synthesis. Although results have been slow to come, the team members have not let “any grass grow under their feet” but have been making many difficult synthetic changes to find answers to their difficulties. The outstanding work with ethylene tetrafluoroethylene (ETFE) perfluorinated membranes with grafted functional groups by Varcoe (University Surrey) and Mustain (University of South Carolina) showing 2 W and 5 A/cm^2 gives incentive to continue this work to make a stable fluorinated AEM.
- The team is examining new anion-exchange polymers as membranes and electrode binders for alkaline fuel cells. The project is a collaborative effort with the National Renewable Energy Laboratory (NREL) (the lead organization), Colorado School of Mines (CSM), University of Tennessee (UT), and Lawrence Berkeley National Laboratory (LBNL). The tasks for each team partner are well defined and include polymer synthesis, materials fabrication and characterization, and mathematical modeling. The project is 70% complete. The overall project objective was not clearly defined in the slides, although milestones and go/no-go decision points were listed. No milestones were identified beyond September 30, 2018, even though the project does not end until March 2019, which was surprising.
- The most critical barriers, such as membrane stability in an alkaline environment and anion-exchange membrane fuel cell (AEMFC) performance and durability issues, have been addressed. However, more fundamental barriers for the application, such as the impact of carbonate/bicarbonate formation and its impact on membrane properties, including stability, and on fuel cell performance and durability, have been addressed only to some extent.
- The work addresses the performance and durability of AEMFCs. A PF-based AEMFC provides some potential advantages for phase separation to improve conductivity and for water management. The project still appears to focus on alkylammonium cations, even though the work indicates these cationic groups are degrading and more stable cationic groups have been identified in previous work.
- Go/no-go criteria of ≤0.1 ohm cm^2 is five times the polymer electrolyte membrane (PEM) target, with no plans or approach shown for how to reduce it further. It is not clear how to assess whether the technology will be competitive with PEMs. The approach of using accelerated ex situ tests is good. The project focuses

on using temperature as an accelerating factor; the team needs to validate whether 140ºC is too big of a hammer or whether the results correlate with in situ testing. Also, the team could consider low relative humidity (RH) as another option for acceleration. There is no clear approach to improving quaternary ammonium (QA) stability. CO_2 cycling is a good approach to assessing the CO_2 tolerance. The approach to focus on the impact of electrodes on water management is good—which is critical for AEMFCs. It is unclear how AMFC modeling will affect materials development.
- The project is focused on the major issues of AEMFCs, including performance, durability, and air tolerance.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The work by NREL looking at water management in AMFC systems has led to significant performance improvements. The ETFE-based electrodes prepared with the solid ionomer powder method have shown good improvements. Durability has improved but is still an issue with the materials shown. The project has met its performance milestones to date. A performance milestone is upcoming for the Gen 3 polymer, but insufficient data indicating the status or progress toward that milestone was provided.
- Very good progress has been made in terms of demonstrating high power density. Very good work was demonstrated, and many useful insights were generated through the comparison of the different electrode preparation processes and the impact on performance. However, the different behavior cannot be fully understood, especially when comparing to the results of FC-146. The results regarding the back diffusion of water and the related flooding issue are also important.
- The project showed impressive progress in many areas.
- There have been many unexpected problems during this project, but the team is working to resolve them. The ETFE work gives hope for fluorinated AEMs, but “the jury is still out.” The team’s modeling is showing that carbon dioxide from air may be a “show stopper” for an AEMFC in air. However, a fluorinated AEM may have uses outside of fuel cells or possibly in a fuel cell with a bipolar membrane that uses the fluorinated AEM (see Sikan Peng, “A self-humidifying acidic-alkaline bipolar membrane fuel cell,” *Journal of Power Sources* 299 (2015): 273–279, doi:10.1016/j.jpowsour.2015.08.104).
- Progress has been satisfactory, although somewhat slower than expected based on the qualifications and experience of the research team. Too much time and emphasis were placed on a durability test that is not used by the AEM community and that has not been sufficiently correlated with simple high-temperature alkaline soaking tests that are used by the majority of AEM researchers. The Gen 2 polymer did not work well as an electrode binder compared to an ETFE material that has been developed and tested by others. Fuel cell tests with a PF-AEM catalyst-coated membrane were lackluster. The modeling work was satisfactory. The issue of carbon dioxide build-up in recirculated hydrogen was brought up but not addressed. There was insufficient comparison of the principal investigator’s (PI’s) AEM(s) and those in the open literature. There was no clear advantage presented in the PI’s films in terms of enhanced transport or mechanical properties or in the polymer’s chemical stability.
- The project is barely meeting not-so-challenging area-specific resistance (ASR) targets, with no clear plan for further reduction. The results to show improved stability of tether are good, but QA degradation is still a big problem. Testing and models confirm that carbonate is a big issue, but no materials of operating strategies were proposed to address this—it looks to be a fundamental issue with QA-based AEMFCs. There are major issues with the PF-AEM electrode used in this study, especially in terms of stability. It is unclear whether this is a fundamental issue with PF design or whether some of the issues could be resolved with optimization. All performance data shown was in oxygen—not air—with high loading platinum catalysts. The stability of the Gen 2 AEM/ETFE system was shown for only 15 hours in H_2/O_2—and performance was nowhere near the target in those tests. It is unclear how AMFC modeling is being used to support development; there is no model validation with data.

Question 3: Collaboration and coordination

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

- This collaboration of NREL, LBNL, Oak Ridge National Laboratory (ORNL)/UT, CSM, and 3M covers all aspects of the project in a complementary and effective way. The project is also supplying membranes to a large number of others, which promotes the technology.
- The collaborations with multiple project partners are clear and appear to be productive in all cases. Additionally, there are obvious significant collaborations with others outside the project.
- The collaborators and their roles are clearly defined, and the most important universities, laboratories, and companies that can contribute to the project's success are involved.
- Collaboration is evident with others in the AEMFC community, and NREL has provided a service to the community by providing their Gen 2 membrane to others working on AEMFC catalysis. It is not clear how the modeling results are affecting the rest of the effort. The interactions have appeared to be one way: the experiments provide data to the modeling effort. The project team has not shown evidence that modeling is providing any guidance or suggestions for improving the experimental effort (e.g., for water or carbon dioxide management).
- The contributions from CSM and UT were not explained or presented. Most of the presentation was focused on small molecule chemical stability and membrane electrode assembly (MEA) fabrication, testing, and modeling. It was unclear if/how the modeling results were influencing the direction of the experimental work. The modeling work has not provided new information that would help the PI to synthesize new polymers and fabricate new membranes with a preferred set of properties and/or a particular structure.
- It is unclear how LBNL modeling work fits in with the rest of the project, whether the project team could meet project milestones without this modeling work, or which results—if any—came from CSM and ORNL/UT.

Question 4: Relevance/potential impact

This project was rated **3.1** for its relevance to/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 has made great strides. There is no "payoff" yet, but it would be a reasonable approach to lowering costs if using non-PGM catalysts in liquid alkaline translates to AEMFCs. However, this team suggests that carbon dioxide from air may be a "showstopper" for use of AEMFCs in air.
- There is a need to examine/develop alkaline fuel cells that produce high power without the use of precious metal catalyst electrodes. The PI is investigating new AEM polymers with improved chemical stability, which is important. The team is also modeling water transport in an operating MEA, an issue that needs such attention.
- It still remains to be seen whether AEMFCs will have significant impact because, despite the substantial progress, there are still significant barriers to overcome.
- AEMFCs have potential for reversible fuel cells, where pure oxygen generated during the electrolysis step can be utilized in the fuel cell mode, and can potentially enable PGM-free oxygen evolution reaction/oxygen reduction reaction catalysis. The project area, AEMFCs, is not well aligned with the transportation focus of the Fuel Cell Technologies Office. One issue with AEMFCs for transportation is operation with air and the conversion of the membrane to carbonates, which has a large impact on membrane conductivity and performance and requires additional system components to scrub carbon dioxide from air. Other issues include hydrogen oxidation reaction performance (leading to use of PGM-based catalysts with higher loadings than polymer electrolyte membrane fuel cell [PEMFC] anodes) and lower power densities than PEMFCs.
- It is difficult to assess relevance without a targeted application. Assuming it is automotive, the relevance is fairly low, as the trajectory for system cost and power density do not match that of PEMFC systems, which will not require CO_2 scrubbing or a complex water management system.

- The project and findings help with understanding the fundamentals of AEMFCs. However, the general feasibility of whether AEMFCs can be operated under ambient conditions and can contribute to reducing fuel cell costs by making PGM catalysts obsolete has not been addressed. Therefore, the progress toward the overall DOE goal cannot be assessed.

Question 5: Proposed future work

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

- The project team has a good plan. One recommendation would be to add ionomer development work based on the obvious challenges with electrodes and catalyst layers.
- The plan on slide 21 is good. The project team should try the Gen 3 polymer as soon as possible. The team should study stability (etc.) and other effects of carbonate and should optimize electrodes and performance with new materials.
- The suggested focus on increased stability is appropriate. More information on which cation groups are going to be pursued would be beneficial. The suggested electrode optimization studies are appropriate. It would be good to integrate PGM-free catalysts in electrode optimization studies, as the thicker electrodes are expected to have a substantial impact on mass transport and water management.
- The proposed future work addresses further important issues such as polymer synthesis, characterization, and modeling. However, the impact on the membrane and the electrodes of more meaningful operating conditions (e.g., varying RH) and temperature conditions needs to be evaluated.
- Specific future work tasks were not given in the presentation. A qualitative list of remaining challenges and barriers were listed. Unfortunately, no property targets or fuel cell performance targets were listed. It is unclear whether the PI will continue to use ETFE as the electrode binder. It is unclear whether there is any compelling reason to use the PI’s polymer membranes versus existing AEM films that are well described in the open literature. The technical target for future AEM/polymer stability studies is unclear. The cause of the gap between experimental and modeling results is unclear. The cause of the gap could include physical property data, electrode kinetic data, and/or insufficiently detailed models, but it unclear which is the cause.
- The future work mostly focuses on stability improvement (it is not clear how), diagnostics, and modeling to understand the effect of operating conditions. That is all good, but what is missing are the materials/designs for improved performance. Significant work must be done to show competitive performance with PEMFC systems—even without CO_2. All data shown were in oxygen—not air—with high loading Pt catalysts.

Project strengths:

- The work on water management has led to performance improvements.
- The project’s strengths include access to promising materials, analytic methods, and expertise. The modeling support to understand fundamentals is very helpful. The transfer of knowledge from PEMFCs, such as applying the very good understanding of electrode preparation and characterization methods, is a strength. Support from industry partners such as 3M is also a strength.
- Polymer synthesis, membrane characterization, and fuel cell testing are the strengths and the heart of this project. It is great to see 3M involved.
- The attempts to address many of the major barriers represent a project strength. Other strengths include excellent collaborations, clear presentation of results, and not overselling or exaggerating results.
- The project addresses an important subject, that being the development and testing/evaluation of polymeric materials for the membrane and electrode binder in alkaline fuel cell MEAs and the modeling of MEA performance/behavior during fuel cell operation.
- This project contains a good balance of experimental and theoretical/modeling work, although it would be beneficial to see these better linked. The robustness of PF ionomer backbone and tether, as well as good water transport properties, provides a promising concept for continued development. Only the AEM did not ignore the effects of CO_2. The team should consider water management in the design and materials selection.

Project weaknesses:

- The project team should devote some more effort to electrode development instead of simply relying on high catalyst loadings.
- The modeling has given some insights, but these insights seem to be premature until a good polymer is found to model.
- It is unclear how the modeling activity is driving development work. Project technical targets are defined to move the bar, but there is no clear definition of what would be required for original equipment manufacturers to consider implementing the technology. All testing is still taking place with oxygen, not air. All stability testing is in a steady state.
- The project continues to use alkylammonium cations that are degrading when the project team knows of more stable cationic groups.
- The PI's degradation test for Gen 2 and Gen 3 anion-exchange polymers is non-standard and not linked to conventional membrane/polymer durability tests in the literature. It is unclear how the PI's new polymers compare with AEM materials in the open literature. The performance of the PI's polymers as electrode binders in an alkaline fuel cell MEA is inferior to that of an established ETFE polymer (from Varcoe's group at the University of Surrey). The PI and the team have not presented an experimental plan to address this shortcoming. The PI indicated that the build-up of carbon dioxide in a recirculating hydrogen feed stream will be a significant problem during alkaline fuel cell operation, but no solution to this problem was indicated in the future work.
- The project cannot contribute to answering the question of whether the fundamental problems with AEMFCs (e.g., carbon dioxide, anode kinetics) can be overcome.

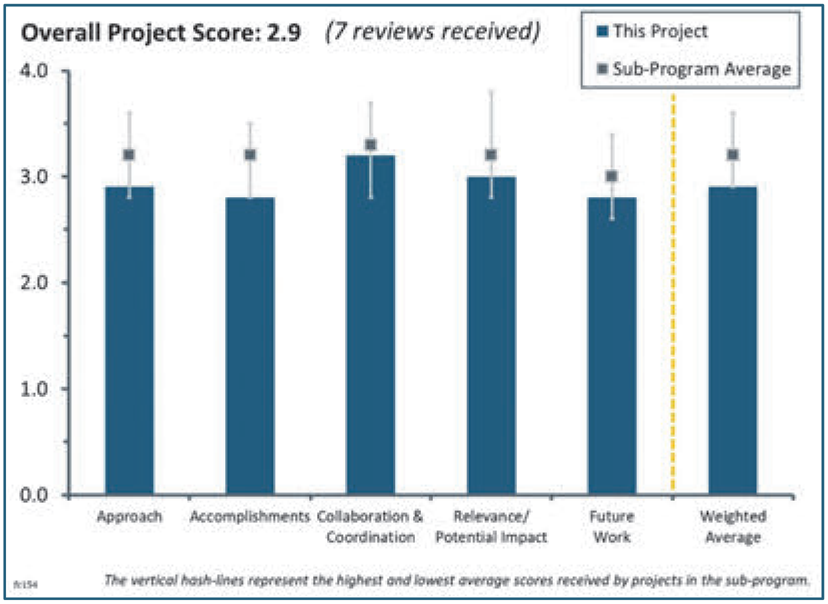
Recommendations for additions/deletions to project scope:

- The project team should set specific performance targets for the membrane and binder. The team should provide more information and results as to how the collaborators at CSM and UT are contributing to the project. The team should link the PI's durability test to the alkaline solution soaking tests that have been used by others. The PI must decide and explain whether the team will use ETFE or PF-AEM as the electrode binder in fuel cell MEAs.
- The team should keep working to further reduce ASR. The project should include validation of ex situ stability tests with in situ data. It is recommended that the project conduct performance testing in CO_2-free air and run stability tests longer than 15 hours. The project team should make sure to tie modeling work to materials development and consider the cost of concepts in materials/design selections.
- The team should investigate the stability of membranes and electrodes under more relevant dynamic conditions (temperature, RH changes) occurring during fuel cell operations. In addition, the impact of lower PGM loadings should be addressed in more detail.
- The team should focus on the Gen 3 polymer, interact with LANL group on side chains, and focus on stability, which is still a big question.
- The team should add ionomer development to the project scope. An AEM ionomer could be beneficial to all AEMFC developers.
- Some work with PGM-free catalysts in the water management work could be beneficial.

Project #FC-154: Fiscal Year 2016 Small Business Innovation Research (Phase II Release 1): Regenerative Fuel Cell System

Paul Matter; pH Matter LLC

Brief Summary of Project:



Fuel cells operated in a reversible manner are a promising potential energy storage solution, but high system cost is a major barrier. Development of a low-cost reversible fuel cell would be a key breakthrough for energy storage. This project, which builds on an earlier Phase I Small Business Innovation Research effort in platinum-group-metal (PGM)-free catalysis, aims to develop and demonstrate a reversible anion-exchange membrane (AEM) fuel cell that incorporates membrane electrode assemblies as regenerative stacks. System durability over 1000 cycles will be demonstrated, and economic analysis of the developed system for use as a grid energy storage technology will be performed.

Question 1: Approach to performing the work

This project was rated **2.9** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project has a clear objective of developing hydrogen and oxygen electrode catalysts for reversible AEM fuel cells, which is well supported by the technical approach. The project has successfully demonstrated 1000 cycles, which is well above the go/no-go decision point of 360 cycles.
- The project is directed at meeting the interim durability target for reversible AEM fuel cells and 1000 cycles at 42% round-trip efficiency by developing low-cost catalysts.
- The project aims to make inroads toward a more stable and cost-effective regenerative fuel cell system by using low-Pt and Pt-free electrodes.
- The approach is well-thought-out and does address many of the critical elements of a reversible system. However, this is quite a complicated "ask," as both galvanic and electrolytic processes are difficult to develop individually, let alone in a single device. The work presented identifies and highlights the areas that need to be perfected as well as what needs to be focused on in future projects. Some are related to the membrane and electrode dynamics, some are related to cell design and costs, and some are related to operating modes.
- The project team selected and combined cathode and anode catalysts as well as an AEM for a reversible fuel cell to improve cost and durability. However, the use of a platinum-free catalyst, which corrodes at high electrode potentials, and an AEM susceptible to carbon dioxide contamination limits the proposed system's capabilities.
- The approach, while ambitious, seems scoped adequately to address concerns about catalysts and cells. While it is dependent on ionomers and membranes supplied by others, for the size, it is acceptable. There is a concern, however, that perhaps the most significant issues are not being explored (e.g., the impact of potassium hydroxide [KOH] and pressurization). It would be beneficial to see the entire load cycle and its derivation, since it is not clear why the charge can be so much lower than discharge, depending on location and load profiles. This should further be used in the technoeconomic analysis to look at different profiles.

- The approach slide does not show technical terms. It is hard to know how pH Matter accomplishes such fuel cell and electrolysis data. The technical work scopes of pH Matter and Giner, Inc. (Giner) overlap. This project looks very challenging because there are not many resources available for reversible fuel cells.

Question 2: Accomplishments and progress

This project was rated **2.8** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project team identified platinum and platinum-free (COR-2, or CN_xP_y) catalysts. The team established the performance of the platinum-free catalyst for different compositions in a cell configuration. pH Matter demonstrated the durability of the platinum catalyst in a half-cell (no appreciable loss in activity). However, the platinum-free catalyst is not stable. The team demonstrated the operation with two different duty cycles and with a single cell and a three-cell stack. The team also demonstrated operation in a commercial electrolyzer with a four-cell stack and a potassium hydroxide electrolyte. Either a commercially available membrane or an unidentified membrane was used. An economic analysis was completed with a National Renewable Energy Laboratory (NREL) model.
- The team was able to develop 25 cm^2 cells that showed high durability for over 1000 cycles and was also able to simulate reversible cell operation for over 250 hours.
- The project has generated significant durability data in single cells as well as in three-cell stacks.
- The project completed the tasks for hydrogen electrode development, oxygen gas diffusion electrode (GDE) development, cell testing, stack testing, and economic modeling. The data on slide 7 shows better performance with a PtRu/C and HE-1 anode electrode than with Pt-Ni nanowires developed by the project partner. The fuel cell performance target was also met with a PtRu/C anode electrode (slide 9) and using hydrogen–oxygen rather than hydrogen–air. It is not clear whether the funding opportunity announcement (FOA) had specified and allowed oxygen as the cathode gas since there are system implications (oxygen storage in addition to hydrogen storage). It is not clear why the durability data in slides 10 and 11 are for low fuel cell voltages. The data in slide 12 indicates significant degradation in fuel cell mode. Slide 14 shows poorer performance in a four-cell stack (2.0 V cell voltage in electrolysis mode) compared to single-cell (<1.8 V cell voltage in electrolysis mode). Clearly, more work is needed in assembling stacks using the cells fabricated in this project. It is not clear what was accomplished in fiscal year (FY) 2018, since five slides (slides 7, 8, 9, 12, and 13) were duplicated from the FY 2017 poster.
- Overall, there were good accomplishments in terms of comparison of performance to baselines. The catalyst loadings, though, are somewhat high, and the baselines used appear to be much lower than state-of-the-art polymer electrolyte membrane systems. There is a concern and lack of clarity as to why KOH is required, and coupled with even the small amount of CO_2 produced, this creates concerns for a closed system that is being used. In addition, issues with parasitic currents could also be a concern with liquid electrolytes. The durability results are promising, although accelerated stress tests could be valuable. There is some question regarding the technical engineering analysis since it compares only a discrete fuel cell and electrolyzer with a unitized reversible stack, but the better comparison would be another technology that is electricity-in and electricity-out, such as a battery.
- The results point to technical areas that need to be further addressed. The accomplishments are positive, yet they are quite preliminary. The initial project targets are preliminary and will need to be reassessed if the technology is to reach a commercial state. More in-depth studies must be carried out in such areas as the membranes (about which, unfortunately, this work provides no information), catalysts, unknowns, and operating modes. These areas must be evaluated and better understood from a fundamental perspective. The cell hardware is also an unknown, and therefore it is difficult to comment on the impact the current design has on performance in this two-way process. The accomplishments must be re-reviewed once the goals and targets are modified.
- The progress of this project is disappointing. Slides 9 and 10 have basically the same data sets from slides 12 and 8 from the 2017 DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR). The previous year's AMR presentation stated the primary focus of this project was to develop electrode material. This year, the objective was changed to "demonstrating 1000 cycles..." Demonstrating over 1000 cycles is a good achievement. Three-cell-stack performance and cycling durability are also impressive.

However, it is unclear why fuel cell performance tested with the stack exhibited poor performance. There are many uncertainties about cell components regarding performance and cycling durability.

Question 3: Collaboration and coordination

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

- The make-up of the team is quite good. It involves folks with knowledge of the critical aspects of any development effort, leading to the commercialization of a technology. It is anticipated that the input from the members will address some concerns: too early, not enough electrochemical and process engineering, and related mechanical engineering to date.
- There is strong interaction with Giner for testing commercial stack design and with NREL for low-PGM catalysts.
- The project has successful collaboration with an industrial partner and a national laboratory.
- There are three partner organizations: Giner, NREL, and Lockheed Martin. The contributions from Giner and NREL are clear. Although the interest in Lockheed Martin is clear, this organization has apparently not significantly contributed during this evaluation period.
- The team is well balanced, with relevant partners providing their expertise. The funding, however, seems to be perhaps insufficient for the partners to be fully engaged. Without a detailed breakdown, it is hard to ascertain.
- It is not clear how NREL's Pt-Ni nanowire contributes to cell performance and durability. Single-cell and stack testing by Giner provided some values, but the data looks different, as NREL uses different component materials and different test protocols. The role of Lockheed Martin on the project is not well defined.
- The FY 2018 poster does not have any slide identifying contributions from one of the partners.

Question 4: Relevance/potential impact

This project was rated **3.0** for its relevance to/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 is a very strategic project, especially with the renewed and growing interest in funding research of reversible fuel cells.
- The development of low-Pt- and non-Pt-based regenerative fuel cells is highly relevant to the Hydrogen and Fuel Cells Program.
- The project aligns well with the Hydrogen and Fuel Cells Program. The research on reversible fuel cells potentially gives much information to the fuel cell and electrolyzer mode. This project is more appropriate as a Fuel Cell Technologies Office (FCTO) FOA project rather than a Small Business Innovative Research project, since there are no standard materials available under high pH conditions.
- This project, especially the lower technology readiness level status, is in an early stage and is well aligned with current DOE objectives. If the technology is successfully developed and commercialized, the impact could be significant if the technology is deemed scalable and used in grid storage and power-to-gas applications. However, it has a long way to go.
- The project objectives are consistent with DOE's mission to develop fuel cell and hydrogen storage technologies. All the results included in the poster were obtained with the COR-2 cathode catalyst that was licensed from Ohio State University (not developed in this project) and the PtRu/C anode catalyst (presumably not developed in this project). The HE-1 anode catalyst also looks promising, but the source is unknown.
- The proposed regenerative fuel cell system has the potential to reduce cost and increase performance for energy storage. However, a carbon-based oxygen evolution and reduction catalyst in an AEM-based system is not expected to be durable because the high electrode potentials will corrode the platinum-free catalyst and the membrane will be contaminated by carbon dioxide in air.
- While the improvements are noted and show promise, there is an overall question regarding how reversible fuel cells are really part of FCTO and a good direction. The analysis, especially with different operating

regimes and conditions, does not address whether a single stack is better than two optimized stacks or other end uses for hydrogen or storage in batteries.

Question 5: Proposed future work

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

- This project touches only on the work that needs to be addressed to result in a commercial device. Membranes must be better understood; electrode composition, ionomers, and electrode structure and stability studies under a number of scenarios must be investigated. Scalability and the impact on realistic and practical applications based on engineering assessments of performance, reliability and, most importantly, economics must be evaluated, but it is too early. Substantially more detailed planning, testing, and development must be part of any future engineering and application activities.
- The team wisely identified the need to integrate with hydrogen economy and grow commercial partnerships as a future path for reversible fuel cells.
- The project ended in April 2018, and it appears that the project was not selected for Phase II extension. Therefore, very general future work is proposed.

Project strengths:

- The primary strength is that the team has touched upon the critical and most important aspects of the technology that need to be developed. The team knows what areas to continue to work on and what needs to be done. This implies the team has the know-how and resources to accomplish the next level of development.
- pH Matter did a good job in testing alkaline reversible fuel cells. The topic area is well aligned with DOE FCTO research subjects. This is a very challenging project because of the limited material availability. The project team's ability to demonstrate >1000 cycles with relatively stable performance is impressive.
- The project has a strong team with good progress on catalysts for AEM electrolysis and fuel cells under relatively benign but still significant conditions and loadings.
- The project team demonstrated 1000 cycles with a Pt-free catalyst. The collaboration with Giner brings demonstrated expertise in regenerative fuel cell systems.
- The project strength is its relevance to DOE FCTO.
- This project is highly collaborative and has an experienced team.

Project weaknesses:

- The project weakness is based solely on the expectations that commercialization of the technology is likely and economical. It is way too early to make any projections until the technical challenges are much better understood and the development path is clear, which is likely to take years. Unfortunately, the reviewer does not have detailed information on the critical components in this project and therefore cannot tell whether those components, individually, will be able to be commercialized as well (e.g., the membrane in this effort is still in a development stage, the catalysts are unknown, etc.).
- The project team had issues related to platinum-free and AEM durability. The other project weaknesses are several tests' use of KOH, which is not entirely relevant to an AEM technology because results may not be applicable or the test plan may ignore component integration (the existence of interfacial resistances); the small stack size, which could mask flow distribution and heat transfer problems between individual cells; and the apparent absence of integration for the Lockheed Martin team members.
- The current status of the technology project has an unrealistic stack lifetime necessary to provide high value. The project needs further materials research and stack design to increase the attractiveness of this technology for grid storage applications.
- The project has uncertainties about the use and function of KOH that may limit the applicability or knowledge.
- The project has not made much progress since last year. The poor cell performance in the electrolyzer mode needed to be identified before cell testing. The material availability for this project is a substantial

problem to demonstrating good cell performance. There is not a knowledge-learning process from this project. Overall, the partnership is weak.

Recommendations for additions/deletions to project scope:

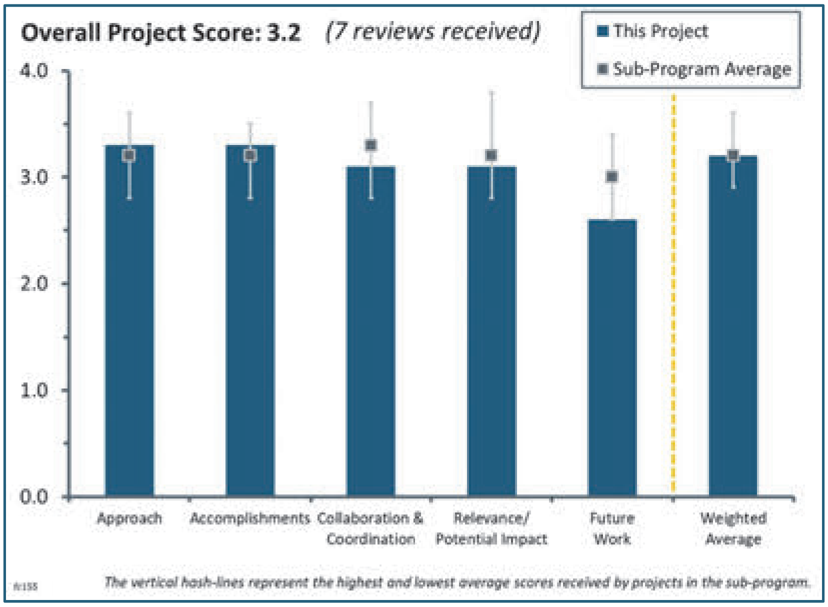
- The project team needs to find the alkaline membrane, ionomer, and catalyst supply unless pH Matter has some potential materials to use. Also, the team needs to show a clear pathway of how this technology can ever be commercialized. Last, the team needs better-defined short-term and long-term targets.
- The project team should investigate what the economics and engineering requirements are for the storage application and then look at the technology under development. Additionally, the team should add in-depth analysis tasks for the membranes, electrodes, process engineering, cell design, and of course, much longer testing, cycling, start–stops, reliability, and costs (including stack life). It does not make sense to compare costs to automotive components, as the lifetime and performance expectations are totally different. The team should reassess such evaluations.

Project #FC-155: Novel Ionomers and Electrode Structures for Improved Polymer Electrolyte Membrane Fuel Cell Electrode Performance at Low-Platinum-Group-Metal Loadings

Andrew Haug; 3M

Brief Summary of Project:

The objective of this project is to develop novel ionomers and electrode structures to improve polymer electrolyte membrane (PEM) fuel cell performance and durability. The focus of the ionomer development will be on combining high proton conductivity with improved oxygen transport. The project also seeks to understand and optimize novel cathodes that utilize nanostructured thin film (NSTF) catalysts in powder form. These powder catalysts will be integrated with the ionomers to develop an advanced cathode of high activity and durability. State-of-the-art novel characterization and modeling techniques will be used to guide these development efforts.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project focuses on overcoming cathode transport limitation using dispersed NSTF and novel ionomers. The project clearly addresses the following key barriers identified by the Hydrogen and Fuel Cells Program (the Program): cost, durability, performance, and operational robustness. The targets set for the project with respect to the catalyst, support, and membrane electrode assembly (MEA) are clearly laid out and meet or exceed the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRDDP) targets. The approach of dispersing NSTF has the potential to change both the NSTF paradigm (lacks an ionomer, prone to flooding electrodes), while also changing conventional Pt/C-based electrodes by having supported catalysts of unique aspect ratios. The use of novel ionomers is welcomed, as well, which can move levers around O_2 permeability and H+ transports (thereby reducing the ionomer content). It is not clear why particular ionomers (perfluoroimides) and multi-acid side chains (MASCs) were chosen, why it is assumed they would move properties in the desired direction, and how they are different from the 3M725 and 825 chemistries.
- In principle, NSTF could be an ideal extended-surface object for incorporation into a dispersed catalyst layer. The idea has existed for a while, and it is good to see this project funded. Hopefully, specific activity is much higher than for nanoparticles. The project designs the approach by focusing on what happens at the ionomer–platinum interface, which is reflected in the measurements of oxygen permeation and proton conduction through ionomer. These characteristics are also mentioned in the two go/no-go decision points. However, not much is mentioned about the catalyst layer design as it pertains to Fickian mass transport losses; it would be easy to imagine a very compressed layer of NSTF objects with little porosity. The project is more proactive than past NSTF projects in addressing conditioning and robustness. This needs to be encouraged further.

- The project approach involves two main thrusts: the development of improved electrode ionomers with higher oxygen permeability and higher proton conductivity, and the development of new electrode structures based on dispersed NSTF powder. Both thrusts are highly relevant and hold promise for enabling improved fuel cell performance and durability.
- NSTF continues to offer promise for high activity and durability. This project is looking at novel ionomers in electrodes and using NSTF in a dispersed nature; these approaches are of value. The synergy between the two approaches, if it exists, is not clear.
- The approach is very well planned to demonstrate relevant technical targets at the end of the project.
- Modifications to the basic ionomer are important to improving performance at low loadings; however, it is not clear how/why an imide-based functionality will lead to higher permeability. Ever since NSTF first came out, people have been asking 3M to try it as a powder, so it is interesting to see them do so. However, 3M does not report on whether this is at all a cost-competitive method.
- The idea of enhancing performance by removing the barrier to oxygen diffusion is based on an ideal situation of NSTF catalyst layers and well-defined ionomer coatings. After mixing and coating electrodes and deposition, the actual structure is far from ideal, making this starting point uncertain.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Excellent progress has been made for the project's end goals and targets. All milestones and go/no-go points to date have been met or are on track, and progress has been made. This is indicated by clear metrics summarized in the table on page 5.
- The project has produced a significant amount of data regarding novel ionomer development, characterization, and implementation in fuel cells.
- Advances in Tasks 1 and 2 have been meaningful. Studying the importance of deposition thickness and evaluating several different catalysts and electrode ionomers provided value. The performance and durability obtained have shown promise. Transition metal leaching issues seem more severe than would have been expected.
- A significant amount of work has been achieved in sufficient detail for the synthesis and characterization of the electrodes. Through these results, progress is clearly visible, albeit not always in correlation with the expected outcome.
- The ionomer development work has been highly successful in terms of meeting and exceeding goals and showing substantial improvement in both oxygen permeability as well as proton conductivity versus the baseline 825 equivalent weight (EW) ionomer. The incorporation of ionomer thin film studies at Lawrence Berkeley National Laboratory (LBNL) has been helpful in building an understanding of the reasons the novel ionomers show improved permeability. The ionomer conductivity measurements are useful for direct quantification as well. Durability of the ionomers, and especially possible catalyst poisoning due to ionomer degradation products, is the largest concern. Some data were shown on the electrochemical surface area (ECSA) change during the catalyst accelerated stress test (AST) for perfluorosulfonic acid (PFSA) versus imide ionomer, but it would be good to see more data about changes in mass activity and high-current performance after the AST as well. Though high-level numbers were shown in the summary table (which indicated potential problems with durability), a more detailed discussion and a direct durability comparison with baseline ionomers should be included next year. The dispersed NSTF work is a promising approach, but so far, the encouraging results with the 10Pt/10α NSTF have not enabled high performance at high current. Durability is also a concern with this material. While the ECSA loss during the catalyst AST was shown to be low, the loss in performance at 0.8 A/cm^2 appears to be over 100 mV, far exceeding the DOE target of 30 mV.
- There is nice progress toward DOE and internal targets. It is uncertain how the team is addressing or characterizing the ionomer stability other than through MEA aging performance. The ionomer work is substantial, as the team continues to lower EW while maintaining viability. Just reducing the break-in period for NSTFs has made this work worthwhile.
- The presentation slides appear to contain numerous errors, including a few places where it is unclear whether the liner loading is meant to be expressed in micrograms per square centimeter or milligrams per

square centimeter. The DOE-supported AST data contains an error in experimental design. MYRDDP Table P.2 shows that the current density at which performance losses are to be measured is 1.5 A/cm^2, not 0.8 A/cm^2. The investigators should take notice. It is also unclear what is meant by “Meets metal AST targets.” The performance loss at 0.8 A/cm^2 for the electrocatalyst AST (for 10Pt/10α) is approximately 100 mV, not <30 mV, as targeted by the test. It appears that at 0.125 g/kW, the 10Pt/10α sample is at Q/ΔT = 2.36 kW/K (0.61 V at 80ºC). This should be noted as being a higher Q/ΔT than that at which the g/kW metric should be reported. Robustness testing has passed the targets, but it appears this may need to be repeated for most stable NSTF (with α). It is good to see a focus on conditioning time noted in the technical backup slides. This needs to be repeated for the most stable NSTF.

Question 3: Collaboration and coordination

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

- This is mostly a 3M project, but that makes sense, given that 3M is the most appropriate organization to perform the work and has the capabilities required for most of the key tasks. The limited interaction with Tufts University and Michigan Technological University (MTU) appear helpful, if not entirely critical. The Fuel Cell Consortium for Performance and Durability (FC-PAD) interactions with Oak Ridge National Laboratory for microscopy, and LBNL for ionomer thin film studies, also appear helpful.
- Collaboration with two academic institutions and capable FC-PAD laboratories is a big advantage for the successful completion of the project. So far, contribution from the partners is very good.
- The team members, plus FC-PAD, are all excellent and appropriate. A clear connection with FC-PAD laboratories was highlighted in the work presented.
- There are no doubts about collaboration, although progress in making a (predictive) model seems slow and unconnected.
- This is clearly a 3M-dominated effort; however, there is nothing wrong with that if they have the majority of the tools that they need. The team could aid in the presentation if the slides where the collaborators provided the data show this. After slide 1, only the 3M logo is seen on each page, making one think that all the work was done by 3M; if this is not true, that particular detail should be changed.
- It seems a bit unclear how the collaboration with MTU will contribute to meeting the project goals. The measurement of the ionomer contact angle is interesting, but the project leaves uncertain what the desired contact angle is. Advances in the project appear to be occurring without a validated model. The model is being developed in parallel, but it appears the project could continue without it. Tufts University appears to make some contribution on Task 1 with ionomer conductivity measurements. FC-PAD provided some interesting images to help explain ECSA loss at different liner loadings. FC-PAD could probably be used in more areas of the project.
- The extent of collaboration is not clear from the presentation. It appears as if the work is siloed off. Minimal work from Tufts University is shown, even though the sole publications appear to be authored and funded from that institution. It is unclear how FC-PAD work is being integrated and what the MTU work/impact is. The goals were written as though advanced characterization and modeling would be used to guide experiments.

Question 4: Relevance/potential impact

This project was rated **3.1** for its relevance to/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.

- Work on improving transport and performance in electrodes is extremely relevant to Program goals. There is some reason for concern that the addition of ionomer to NSTF-based electrodes will cause new transport barriers associated with ionomer thin films, but given the known breaking and robustness issues with conventional NSTF, this is a highly logical approach to adapting NSTF, making it relevant for automotive applications.

- Lower EW ionomers with higher permeability will always aid in performance. Extending the promise of NSTF over more operating conditions with less break-in is also helpful and is seen in the good work toward making power metrics.
- The project is addressing important barriers such as cost, durability, and performance through the development of novel ionomers and is integrating them with powdered NSTF catalyst in fuel cell MEAs.
- The project is looking to take on the highest concerns of DOE targets and commercialization. Increasing mass activity and enabling improved water management remain challenges, but the NSTF approach has shown promise in addressing these challenges, and progress in the last year has been good. Novel ionomers also offer potential advantages in performance, particularly in local transport resistance. The results shown suggest improvements may be made. More durability work on the ionomers and addressing the transition metal leaching are both areas that need further effort.
- The project has the potential to make an impact on MYRDDP goals, technically, as shown by the support and metal stabilities. Some of the ionomer results appear to be promising. The total cost of the dispersed NSTF, even at low loadings, is not really addressed at all. It would be beneficial to have some sort of transportability engineering analysis. As pointed out last year, higher performance would be desirable, as would the reporting of $Q/\Delta T$.
- The NSTF catalyst particles have exceptionally well-defined properties, which are lost to some degree if the layers are not equally well defined to provide clear-cut data to build the model, proving that the initial assumptions are indeed correct. If it is proven that the oxygen permeation is significant and can be reduced, this would be great learning that can be applied to all. However, if this limitation is only relevant in situations with solar energy factors (SEF) <10, and SEF >100 electrodes provide better performance and do not have this problem as a bottleneck, then the reason to study this catalyst's layers is valuable only as a model system.
- Despite the possibility that dispersed NSTF could be a very interesting extended-surface catalyst, the relevance slide seems to present some logical inconsistencies. Literature data are shown that clearly indicate that NSTF avoids the trend of ionomer-containing catalyst layers decreasing in performance at low roughness factor. However, this project wishes to disperse NSTF into a catalyst layer with an ionomer. Unless there is some enhancement in the roughness factor (without increasing loading), this may simply cause NSTF to fall into the same tradeoffs familiar to dispersed catalysts. Targets for performance, robustness, and various ASTs well represent the metrics needed to understand the technology's promise.

Question 5: Proposed future work

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

- The proposed future work will help overcome some of the barriers in achieving higher fuel cell performance.
- The future work could be more detailed, and durability should be more thoroughly addressed, but overall, the work appears appropriate.
- The team continues to innovate and try new ionomers, which is good, but it would be helpful if there were an underlying fundamental approach. The majority of gas permeability is in the water phase, so changes in the backbone are unlikely to lead to big changes in gas permeability. The team is trying to reduce the equivalent number of NSTF layers required, but it is difficult to judge whether 10 layers is the right number. It is unclear what the team is driving toward. The team members are, no doubt, doing the economic analysis, but it would be good if they shared what they believe is the final acceptable endpoint, whether it is 5 or 10.
- NSTF alloy integration is considered "critical"; however, it might be wise to consider whether durability, high-current performance, and conditioning are more critical. Certainly, the alloy would help with drive cycle efficiency, but cost and durability, not efficiency, are the major barriers to commercialization. Most of the future work focuses on transition metals. "TMI" as an acronym is not well defined. Some of the project slides need to do a better job of spelling out acronyms and other internal project terminology. Some of the presentation is written in code.
- It is hard to follow some of the details and future work activities, especially when looking at the project holistically. Use of alloyed catalysts seems to be desirable to achieve goals; however, the goals were to use advanced ionomers to do that, not new catalysts, and catalyst processing. It is unclear how FC-PAD

capabilities and knowledge will be leveraged in the future. It is unclear how the new ionomer-swelling issue will be addressed. If the catalyst layer swells, it will negatively affect oxygen transport and water removal, not to mention structural stability.
- Many activities are summarized as optimization, while a degree of unforeseen issues is clouding the structured approach. The anticipated model as a predictive tool may not be finished in time to help identify the right direction to obtain best-in-class results quickly.
- Future work largely continues the approach applied to date, in some cases combining the efforts from the specific tasks. It is not clear how, or if, there will be synergistic advantages (or potentially disadvantages) in combining the NSTF approach with different ionomers.

Project strengths:

- The concept of dispersing NSTF objects has long been sought as a possible high-specific-activity catalyst with water management advantages. It is good to see the concept being developed. The project has placed greater emphasis on conditioning and robustness and has the resources at 3M for industrial scale-up. 3M is very experienced in fuel cell catalyst development.
- The ingredients of this project are strong, both in terms of the catalyst and ionomer, as well as the tools for characterization and presentation of results. There is high potential, provided the initial assumptions that oxygen permeation causes great resistance in this situation (SEF <40) are true.
- The main strength of the project lies in the potential impact of a dispersed NSTF-based catalyst layer utilizing a game-changing ionomer. There is a potential overall impact from leveraging collaborations and FC-PAD.
- The project contains best-in-class performance and the best ongoing work being done in the field on pushing ionomers. There is good durability being shown on NSTF catalysts; making a powder is addressing some of the project’s shortcomings.
- This project’s strengths are a well-thought-out technical approach and the execution of proposed research and collaboration with academic partners, as well as with FC-PAD consortium member laboratories.
- Dispersed NSTF and alternate electrode ionomers are both highly relevant research topics. The team and unique materials are excellent.
- 3M has excellent capabilities for developing novel ionomers and novel electrode structures based on NSTF.

Project weaknesses:

- Work pertaining to layer development will likely stay confidential and will be difficult for others to reproduce. The project may place too much emphasis on alloys versus making sure the Pt/α system achieves durability, robustness, and high-current-density performance targets. The presentation slides need to be more refined. The project is somewhat depicted in code, with easily identifiable mistakes apparent. Some of the material appears to have been assembled in a hurry. Modeling work needs to be better incorporated into the tasks necessary to meet targets.
- There does not seem to be effective collaboration between FC-PAD and its prime contractor and subcontractors. The approach seems to be to do whatever it takes to meet targets without a well-defined procedure. There is a lack of use of modeling and advanced characterization to accelerate innovation or understanding.
- The link between NSTF and novel electrode ionomers is not clear. It seems unlikely that there is a synergistic benefit to looking at both issues in the same project, although both merit investigation individually.
- Within the constraints of the mentioned catalyst and ionomers, the project does not necessarily provide a good catalyst layer design for the PEM. The value of a clear model for a defined system could be diminished if the results do not show correlations in the results because of many other factors influencing performance.
- The slides were presented well, but they are hard to follow when reviewing after the presentation because of poorly labeled figures and undefined non-standard acronyms.
- It would be good to see the philosophy of increasing permeability. The reviewer cannot judge whether the NSTF powder can be made economically.
- The project needs a cost analysis of the novel ionomers.

Recommendations for additions/deletions to project scope:

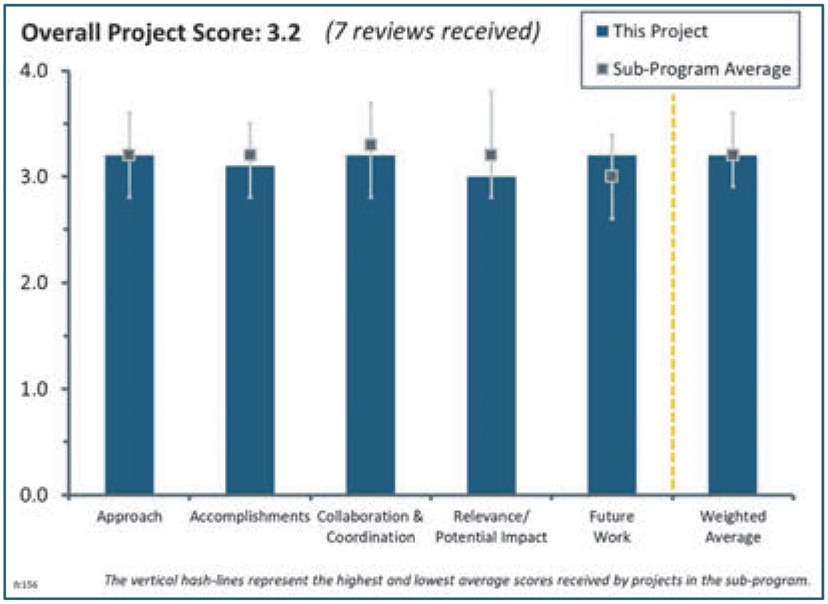
- An added emphasis on robustness and conditioning, especially for best-in-class materials, is always welcome. Robustness and conditioning represent some of the issues that have prevented commercial systems from using NSTF. Catalyst layer thicknesses were not clearly shown in the presentation. It would be interesting to see an elemental mapping of catalyst layers to see how well the ionomer is distributed and whether there are performance improvement opportunities.
- Slight modifications are necessary to cell testing and the reporting of results in areas such as impact of the ionomer-to-carbon (I/C) ratio on fuel cell performance and durability, as well as the impact of the I/C ratio on the electrochemically active surface area. Overall, this is a very solid approach with good results.
- Results (both positive and negative) should be clearly linked to the factors responsible, thus creating insight, in addition to the large amount of data presented.
- It would be good to see some work in characterizing ionomer durability. The wisdom of introducing Ru is questionable if the project team cannot show stability first.
- The project should add full MEAs using low-loaded Pt/C and in-project developed ionomers. It is unclear whether this alleviates the localized mass transport issue.

Project #FC-156: Durable High-Power Membrane Electrode Assemblies with Low Platinum Loading

Swami Kumaraguru; General Motors

Brief Summary of Project:

This project seeks to improve the durability of a state-of-the-art (SOA) membrane electrode assembly (MEA) by identifying and reducing the stress factors affecting electrode and membrane life. Project tasks include (1) MEA optimization of a low-loaded electrode through down-selection and integration of MEA components, (2) durability studies of the developed MEA, and (3) development of a predictive model for degradation in different operating conditions.



Question 1: Approach to performing the work

This project was rated **3.2** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The approach includes a balance of fundamental materials studies (mostly at the Fuel Cell Consortium for Performance and Durability [FC-PAD] laboratories) and an MEA evaluation of materials, with results fed to models for prediction of durability. The project is evaluating SOA materials and determining how best to combine the materials into MEAs, as well as how to operate the MEAs for maximum durability. The project is not developing new materials, though it is using cutting-edge materials developed outside the project.
- The project is addressing several key issues regarding the performance and durability of non-platinum-group-metal (non-PGM) catalysts for MEAs. The outline of tasks, detailing those initiated and also in progress, is good.
- The project contains a structured approach and a clear definition of the phases with a goal to define benign operating conditions.
- The project focuses on the main issues relevant for fuel cell electric vehicle (FCEV) commercialization. General Motors (GM) brings real-world experience, SOA materials, and integration capability. The only downside to the project is how many different areas are being taken on within. This may be less of an issue because perhaps GM would take on these issues anyway, with the overall impact being a higher cost-share contribution for the U.S. Department of Energy (DOE)-funded effort.
- Overall, the project's approach is good. The project appears to be primarily aimed at identifying operational factors that induce decay with SOA MEAs and identifying operating modes that minimize decay. The use of modeling and characterization is necessary and warranted. One aspect of the approach that could be improved is the incorporation of durability testing earlier in the project and with more MEA types. It appears that the approach during the first year was to identify the MEAs with the overall best performance. It is unclear whether the degradation modes and benign operating conditions identified for this "best performance" MEA will be applicable to a wider range of materials than the GM-specific material sets.
- To achieve DOE 2020 performance and durability goals with SOA MEAs, the approach is well-thought-out. However, a good deal of work on electrode and membrane durability has already been done by previous DOE-funded projects; few models have been developed, so it is difficult to understand the novelty in the approach. Also, some of the stress factors in the MEA mentioned in the study are dependent on how

the MEA is manufactured. Electrode cracks can be controlled by the ink recipe and slow drying, and localized stress caused by fibers from the gas diffusion layer (GDL) can be easily eliminated by prepressing the GDL before the MEA and/or electrode assembly; so the model can be generalized for various MEAs by the catalyst-coated membrane, the gas diffusion electrode approach, or a combination of the two, as in the Mirai MEA.

- The approach is generally good, but some improvements are possible. The approach should not be to define benign operating conditions but rather to map out the effect of operating conditions. Original equipment manufacturers (OEMs) can then determine the tradeoffs with the system and the MEA design. Considerable and useful effort was expended to down-select the cathode catalyst layer components. The work was conducted systematically, and useful correlations were obtained. It is not clear what is being referred to in terms of "higher than expected" membrane degradation. It would be valuable to also consider durability aspects for the cathode design. There is a good combination of experimental studies and characterization. The highly accelerated stress test (HAST) work on membranes is interesting and should result in an improved understanding of in situ mechanisms. The fundamental model of mechanical/chemical stress in the membrane will be useful, and an appropriate set of variables has been established, including interactions with the GDL. While the experimental basis for the model is well mapped out, the theoretical basis is not clear.

Question 2: Accomplishments and progress

This project was rated **3.1** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- A high-performing MEA was achieved using conventional approaches via the systematic testing of key materials representing a range of parameters. HAST and shorts approaches for the membrane were developed, which will be useful. There was a nice correlation found for proton transport resistance versus carbon macropore surface area. The characterization of ink structures with different solvent types was useful. There is good characterization of Ce removal from the MEA. The result in the ex situ jig, showing Ce movement by convection, was interesting.
- Excellent progress has been made in preparing and characterizing prototype MEAs with selected catalysts.
- The project is making steady progress in evaluating materials and has produced an SOA MEA with impressive performance levels. The new catalyst supports being incorporated in this project are providing excellent performance and helping to build an understanding of the relevant support parameters that determine oxygen and proton transport resistances, although, in this area, there seems to be much overlap with the GM catalyst project. The project seems to be very helpful in enabling GM to screen materials for use in the company's own MEA development work, but so far, there does not seem to be much learning that could help the community as a whole.
- The project has made good progress in demonstrating a low-loading MEA and meeting DOE loading targets, which also meets the rated power target (but not the Q/dT target at 150 kPa pressures). Additionally, the project has accomplished a good deal of the characterization of the multitude of catalysts, electrodes, inks, and membranes. Development of the Ce migration characterization looks to be a significant accomplishment. It is unclear how this multitude of data at the component level (e.g., ink viscosity) will be utilized toward development of the durability model.
- GM has been able to screen a number of SOA membranes, catalysts, and ionomers to produce the highest-performing MEAs possible. The team has shown good results in terms of achieving rated power performance. These results are clearly relevant for accelerating commercialization. Other efforts are fairly disconnected and, in various cases, have resulted either in meaningful results (e.g., Task 1: relating carbon support type to proton transport resistance, the impact of equivalent weight, etc.) or cases in which the impact of these studies is still undetermined (Task 5: X-ray computed tomography [XCT] for shorting, Ce migration, etc.).
- In comparison with the milestones and tasks listed, the progress and accomplishments are good. However, some of the work done here is already well reported in literature (e.g., the effect of water–alcohol ratio on catalyst–ionomer interaction), so there is no need to "reinvent the wheel." Instead, learnings from published work can be adopted.

- Much work has gone into defining a good baseline MEA using the best selection of materials. Progress was made in improving processes, performance, and the evaluation of defects in the MEA. Very little is shown on the durability, and there are no projections on more benign operating conditions (yet) at this stage.

Question 3: Collaboration and coordination

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

- GM really needs only modest support to execute a work scope like this. The team has leveraged FC-PAD effectively and has small, well-defined roles at the University of Texas at Austin (UT Austin) and Giner, Inc.
- It appears that greater contributions were obtained from national laboratory partners during the past year. This project has a good delegation of assignments for both characterizations and testing.
- Significant collaboration is planned, drawing on key strengths from other groups.
- The project's collaboration appears appropriate and is directly relevant.
- The project is well coordinated with partners and collaborators. Most of the work is performed at GM, but the interaction with Lawrence Berkeley National Laboratory and Argonne National Laboratory for ionomer properties characterization is useful. The extent of interaction with the FC-PAD laboratories so far appears limited because of the lack of a non-disclosure agreement.
- Collaboration with FC-PAD seems very strong and easy to understand, but the roles of UT Austin and Giner, Inc., look very small in the project. GM, as the principal investigator of the project, is doing almost all the work.
- There are no discrepancies or misalignments in the presented PDF.

Question 4: Relevance/potential impact

This project was rated **3.0** for its relevance to/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.

- The relevance for this project is generally high as it pertains to durability in a high-performing MEA design. However, there are concerns about defining a set of operating conditions specific to one MEA type. This will provide one path forward to demonstrate an MEA that meets both performance and durability; however, it may not provide the best overall tradeoff between MEA performance/durability and system design. The approach will also provide useful information that will assist others in design and durability understanding.
- The development and implementation of SOA MEAs is highly relevant to achieving DOE targets and advancing fuel cell commercialization. The topics included go beyond the SOA MEA performance; both Ce and shorting are important and need to be understood. How much impact will result from this project and what will be learned are still to be determined.
- The project is directly addressing key cost, performance, and durability barriers with SOA materials, and it appears that there is a good probability of achieving many DOE targets. However, the impact may be only to the OEM prime contractor and not the industry as a whole, unless additional information is disclosed regarding specific material sets used. It is suspected that this disclosure may not occur, as it may be highly valuable to the OEM for potential future products.
- The project is helping to build an understanding of existing materials, determining how best to combine SOA materials into high-performance and durable MEAs and developing operating strategies to improve durability. This is useful work, but the development of improved operating strategies is highly application-specific; therefore, it is less relevant to the overall DOE Hydrogen and Fuel Cells Program (the Program) compared with new materials development, which can help all applications.
- This project is relevant to DOE's 2020 performance and durability goals, but it is unclear how the developed model can be utilized for other FC-PAD projects or future DOE projects to develop SOA MEAs.
- There is value in making a better MEA and sharing the lessons learned, but perhaps the true benign conditions for operation are obvious. Only in combination with a system running at rated power density or in specific off-spec conditions can major degradation be expected. This is more of a systems control area

for optimization, eliminating extreme conditions. It may prove difficult to identify specifically damaging elements within incumbent fuel cell operation conditions that benefit a greater audience.
- While reversible MEAs have potential applications in various applications, the presenter did not address the issues with meeting DOE targets for FCEV power systems. The team needs to explicitly state the most relevant and critical factors that are being addressed regarding the development of commercially viable devices.

Question 5: Proposed future work

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

- A good plan was presented for the next phase of work. It is imperative to conduct the durability measurements and also support the post-operational materials characterization assessment on degradation processes.
- The proposed future work aligns directly with the project plan, with an increased focus on durability studies and degradation mechanisms via physical characterization and modeling.
- The future work is appropriate for the project goals and objectives. The work has been carefully and thoughtfully planned.
- The plan forward is appropriate.
- The proposed future work looks good and is aligned with project milestones, but the roles of other team members are unclear.
- The project team has excellent intentions, but the net may be cast with too wide a scope to capture all the points mentioned. It is expected that only a few chemical/mechanical stress factors can be investigated.
- The layout of the project over the three different budget periods does not seem to be the most effective for building on advances throughout the project. While the focus on performance in budget period 1 (BP 1) leads in well to BP 2 and durability, the value to the community in developing models in BP 3, and how it connects, is not as clear. It seems it would have been better had this effort been integrated into the earlier efforts so that learning could be applied to the project as it was being executed/performed. All proposed tasks are either good or, at minimum, reasonable.

Project strengths:

- The excellent component and MEA integration and testing capabilities at GM are a significant strength. The access to a broad range of SOA materials is also a major strength since most institutions cannot get access to the best materials.
- This project contains very systematic studies and provides an approach to achieving MEA targets for both performance and durability in the system, although it may place significant constraints on the system. There are good characterization approaches and planned model outcomes.
- The project team has access to SOA materials with good prospects for achieving project performance targets and recognized expertise in component integration into leading MEAs.
- Team strength, materials access, and considerations for system tradeoffs/costs are all strengths of this project. High-performing samples that are relevant for commercial vehicles are also a strength.
- There is a good structured approach that can capture and structure results to provide good learning, coming full circle to operating conditions.
- With GM (industry) as the project lead, along with FC-PAD collaboration, good and relevant results can be expected.
- This is a good, experienced team with members who have performed credibly so far on the tasks identified for this project.

Project weaknesses:

- The total project structure has many activities, too wide a scope, and a long feedback loop, which, in effect, could incorporate all possible activities elsewhere in the process. In this presentation, only the first phase is supported, defining and optimizing the MEA, and no durability or cycling has been attempted. The

reviewer slides state that first, variations and control variables need to be identified to limit the number of relevant options to explore.
- Apparently, the broad scope of activities within this project has delayed converging on an optimized membrane configuration for performance characterization and conducting the durability assessments. It appears that much of the technology is being considered proprietary, which seems to be hampering full sharing of properties with partners charged with the supporting materials studies.
- The focus on tailoring operating conditions, rather than materials properties, to obtain good durability is a slight weakness because of the non-universality of this approach. Within the context of the Program, materials solutions should always be favored over systems solutions.
- The project's relevance to the general community may be low because of use of proprietary materials that may not be otherwise accessible. There are insufficient first-year efforts on the down-selection of durable materials (i.e., down-selection appears to be based on performance only).
- This project may be too specific to one MEA type and may place significant constraints on the system. There is a lack of clarity on model approaches.
- This project lacks novelty in the approach and looks like a consolidation of previous works in an attempt to make it more meaningful.
- The modeling effort could be better integrated into the performance and durability efforts.

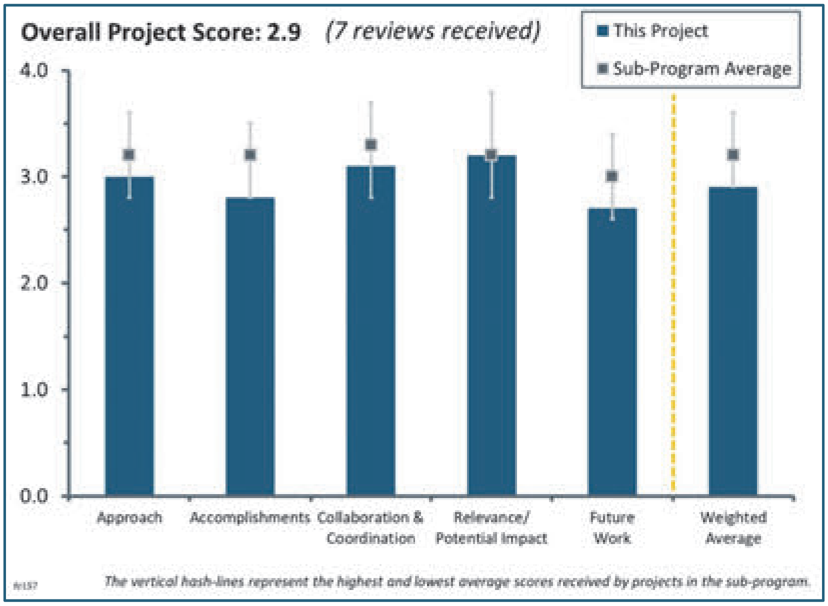
Recommendations for additions/deletions to project scope:

- Overall, the stated plan for future work is strong and should be followed. Emphasis should be focused on identification via device and the materials aspects of degradation processes. However, at the current rate of progress, it seems that objectives related to durability will not be achieved.
- The project has good work and an interesting presentation. It would be good to see similar momentum and direction for the durability assessment going forward. The team must be wary of an anticlimactic ending in the final project conclusions, as operating conditions were not changed from the status quo.
- In addition to SOA proprietary materials, the project should include generally available reference materials (e.g., Pt/Vulcan catalyst) into development and characterization plans, allowing for dissemination of all results.
- The project's scope is appropriate and useful. However, an understanding of the design tradeoffs between durable and high-performing designs would be useful as well, if there is room in the scope for any addition of work.
- The project is extremely broad. It may be better to narrow it down to achieve more depth.
- It is unclear how the developed study/model can be used by other DOE projects.

Project #FC-157: High-Performance Polymer Electrolyte Fuel Cell Electrode Structures

Mike Perry; United Technologies Research Center

Brief Summary of Project:



The objective of this project is to improve the fundamental understanding of transport limitations in state-of-the-art (SOA) membrane electrode assemblies (MEAs) for polymer electrolyte membrane fuel cells and use this knowledge to develop and demonstrate high-performance MEAs with ultra-low catalyst loadings (ULCLs). Transport losses are a major barrier with ULCLs, but fundamental understanding of those losses is currently lacking. To gain better understanding of the nature of these losses in cathode catalyst layers, a detailed microstructure model of the cathode catalyst layer will be developed. This improved knowledge will then be utilized to develop improved MEAs that meet the U.S. Department of Energy’s performance targets.

Question 1: Approach to performing the work

This project was rated **3.0** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project identifies that mass-transport limitations in the electrode are a critical barrier and focuses efforts toward understanding the cause of the transport limitations. The project’s approach is logical and extends current modeling approaches to develop a hierarchical model looking at three different length scales: that of the electrode, the agglomerate, and the catalyst particle. The use of traditional- and non-traditional-type catalysts will test the model’s capabilities. The project is integrated with other Fuel Cell Consortium for Performance and Durability (FC-PAD) efforts. Key to the effort is accurate description, characterization, and control of the agglomerate size. More information on how this will be done would be beneficial.
- The relatively simple approach has already demonstrated correlation with results and validated itself in comparison to published data.
- The design of the approach and organization of the team and resources are well aligned to address the specified problem. Iteration throughout the process will help to refine the model and increase the chances of success. What is limiting is the apparent disconnect between the model development and analysis, and the catalyst development, namely, the non-conventional catalysts. The key accomplishment of the model is the integration of spherical diffusion around the catalyst particles. This is seemingly not relevant for the thin film catalysts tested in this project.
- Modeling projects are always difficult to judge without doing an extreme deep dive into assumptions and methods. The team’s data fits well but, as the presentation speaker said, all models are wrong; this approach will work only if the underlying approach is accurate. In that regard, the project team is not looking at work that General Motors (GM) is doing and testing their assumptions, or modifying a model that may have non-ionomer ionic transport. It is the use of models and fitting that has clearly demonstrated

the unexplained high transport resistance, and now some solutions for it, so it is important to have competing models out there.

- The project is focused on understanding mass-transport losses observed at high current densities (HCDs) for electrodes with low Pt loading through modeling and experimental validation. There are some flaws in the modeling approach, as it assumes a one-size Pt/C agglomerate for catalyst layers with a given Pt loading.
- The approach consists of developing the realistic microstructure model to understand mass-transport losses, which seems very helpful, but the integration of the effect of ink mixing, the ink recipe (water–alcohol ratio, etc.), and MEA fabrication (drying speed and time, etc.) that affects the catalyst layer structure is not very clear.
- The approach of this project relies on having the ability to construct a structure and a fundamentals-based model, identifying the flaw, and then constructing an electrode structure that alleviates the HCD performance loss. It is an idealistic approach that has been tried by other groups in the past seven years and has failed.

Question 2: Accomplishments and progress

This project was rated **2.8** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The modeling efforts have made good progress and have been able to reproduce performance under a variety of conditions. The model reproduces performance losses at low catalyst loadings without having to alter ionomer properties from the bulk properties. The thin film catalysts have been successfully integrated into an MEA. The modeling effort has identified agglomerate size and ionomer equivalent weight (EW) as the two important characteristics to change to improve performance. The performance of the thin film catalysts needs to improve. The model has been validated with both literature results and results at the United Technologies Research Center (UTRC). Experimental work has been slowed by construction at UTRC.
- Progress has been made toward understanding the nature of mass-transport limitations in catalyst layers with low Pt loadings. The proposed hierarchical model qualitatively describes trends in changing transport resistance with Pt loading. Furthermore, the model validation shows that there is no agreement between the experimental results obtained for transport resistance versus Pt weight percent. There is no good agreement between the experimental data for transport resistance versus Pt loading and modeling results, as well. The agreement in the experimental results for Ion Power, Inc.’s (Ion Power’s) low-loaded Pt/C MEAs was good and obtained using the “limited number of fitting parameters,” which usually implies that there were some problems with the physical justification of the model.
- It is hard to judge the accomplishments of this project without many details on how the model is developed, as well as the efforts behind it. It is really good that the model has been validated using literature data and that some progress has been made toward non-conventional catalysts.
- At this stage of the project, it looks like the direction is good with an overlap of key characteristics with the data and model. Further iterations with greater accuracy are expected, as they will enable better discrimination between models.
- The accomplishments associated with the model development have been satisfactory. Incorporation into the overall FC-PAD model is a good result. Progress with University of Arkansas at Little Rock (UALR) catalysts, however, is limited. The cathode results are poor, and it is unclear how they may be improved.
- It is difficult at this point to judge how useful the model is. Its conclusion that smaller agglomerations are necessary does not seem viable on the surface, as so much work has been done on varying ionomer ink structures with very little benefit. It is unclear how the project team’s model fits with the work done by Dr. Y. S. Kim at Los Alamos National Laboratory (LANL). The Pt directly on the microporous layer has a long way to go, and it is doubtful that it will amount to much. That particular structure is too poorly defined to be much of an aid in modeling. Also, even though performance is awful, it is unclear if the project team’s model can predict that it would be so.
- There were only two accomplishments this year: development of the model and testing of UALR’s Pt thin film electrode. The project is not on track. It is unclear how the project will meet its milestone.

Question 3: Collaboration and coordination

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

- This project contains good collaboration with industry, universities, and national laboratories through FC-PAD.
- The organization and feedback structure of this project are excellent.
- This project is a well-coordinated effort between the team members.
- It seems like good teamwork is going on within this limited consortium.
- Collaborations with Ion Power and UALR are working well. Collaboration with FC-PAD partners at LANL, Lawrence Berkeley National Laboratory (LBNL), and Oak Ridge National Laboratory is evident. Additional collaborations for characterization of the electrode structure may be beneficial (e.g., Argonne National Laboratory with X-ray nano-computed tomography [nano-CT] efforts for characterizing pore structure, carbon, catalyst, and ionomer thickness).
- It is doubtful that the structures being generated by UALR will lead to either a compelling catalyst or an aid in modeling. At best, the team will have something like 3M's old nanostructured thin film catalyst, and they have reams of data to model that system. It is unclear what the difference is between the UTRC and LBNL models; if it is just dimensionality, it is not clear why LBNL is not doing all of the modeling.
- The role of each partner is clear, but it is unclear whether Ion Power has the expertise in electrode development to deliver the required structure that the project itself set up. Collaboration with FC-PAD is limited.

Question 4: Relevance/potential impact

This project was rated **3.2** for its relevance to/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.

- The project is relevant to the Fuel Cell Technologies Office, as it addresses the cost barrier for fuel cells. The project directly supports the current focus to improve high-power performance of fuel cells to decrease cost. The potential impact is significant. Addressing the transport limitations could lead to large improvements in power density, resulting in large cost savings.
- The seemingly simple approach in the model appears powerful in explaining results. This insight could easily be adapted for the toolbox of other projects.
- The HCD performance leads to large cost savings.
- A better understanding of transport at low loadings is needed, and the team's model may help this effort. The project team's use of past and published data is good, and it would be nice to see the team continue this effort with GM's current data, as well as Dr. Pintauro's interesting structures, and 3M's work with single-layer planar MEAs and mixed-layer MEAs, or the National Renewable Energy Laboratory's extended surfaces. The model would be useful if it would be resilient over numerous structures, and there are plenty like this out there already.
- Addressing HCD performance limitations is key to decreasing stack cost. There still remain questions as to the true source of these limitations at low-platinum-group-metal (low-PGM) loadings over the many length scales present in the MEA. Optimization and refinement of a catalyst-layer transport model and incorporation into the FC-PAD model will provide important insight.
- HCD performance is limited by mass-transport losses for low-PGM electrodes, so understanding the mass-transport losses using microstructures is important. This will help achieve the DOE's research and development goals. However, model validation for various catalysts needs to be done to make it more meaningful. One or two carbon supports with a Pt-only catalyst may limit the model's potential.
- The model needs to be improved to make an impact on technology development for fabrication of catalyst layers with low Pt loading.

Question 5: Proposed future work

This project was rated **2.7** for its proposed future work.

- The proposed future work of looking at variations in ionomer EW is logical, and the model predicts improvements after decreasing EW. The plans to modify the model for the thin film catalysts are appropriate. The plans to try to vary agglomerate size are not well defined, and it is not clear what variations will be achievable.
- The proposed future work is focused on MEAs/cathode catalyst layers (CCLs) with conventional catalysts, but model validation and demonstration using one of the SOA catalysts developed under other DOE-funded projects would be useful.
- While the proposed future work is relevant and obvious, how the project team will get there is not as clear. The explicit impact of the model is not defined, at least in the presentation. Specifically, it is not clear what changes are to be made to the CCLs to attain improved performance. Future work includes model development for the thin film catalysts but does not explicitly state how the team proposes to improve the MEA performance of the thin film catalysts. If this cannot be improved, then development of the model is not necessary.
- It is hard to understand whether the ultimate goal is a better model or an optimized MEA from using the model, or if the optimization will prove the model. Some of the team's optimization regarding ionomer–carbon ratios (I/C ratios) and EW is very easy to change and should be done. It is unclear what benefits the additional catalyst structures will provide and whether the model suggests that this will help. It is uncertain if this will help to validate the model; if so, and it is over a structure that has no relevance, perhaps this is not needed. There are plenty of additional interesting structures already developed in the public domain that the team can use to validate the model.
- There is no distinct separation between the MEAs made for optimizing the model and the MEAs that will achieve the target, while it is inherently implied that understanding from a (finished) model is key to achieving this target. It appears that the iterative cycle will be continued until project funding and time run out. The criteria and objectives could be more defined as steps in this process.
- The project plans are built on past progress and are too broad, not providing any specifics of the proposed work. No path is proposed in the future plans regarding the improvement of thin film catalyst layer performance.
- It is unclear how the project intends to meet targets.

Project strengths:

- The project provides a unique point of view; the model appears to be able to predict performance using bulk properties (which are readily measured) and does not need to vary properties with thickness of the ionomer.
- The project contains strong collaboration among team members, and the principal investigator and the team are experts in the field. The microstructure model development at three different length scales is another strength.
- The team has strong modeling capabilities, and the proposed novel modeling approach allows one to examine mass-transport limitations from a different perspective.
- This is a very strong team with a wide breadth of experience and capabilities. There is good collaboration to generate MEAs and collect data to put into models, which seems like an effective loop.
- A clear approach has already delivered a positive correlation, and the project partners seem aware and capable of addressing all anticipated issues to make the MEA and model more sophisticated.
- The strength of the project lies in the incorporation of spherical diffusion into the general CCL transport model.

Project weaknesses:

- To this point, the model has not been tested over many different ionomers, catalysts, and catalyst contents, though some of that is planned. It seems much more could be done by fitting to data by others, including what must be a huge archive of UTRC and LBNL data. For example, dozens of I/C ratio studies have been done, which usually show a rather subtle effect over a given range. The team seems to predict that it could lead to a large improvement.

- The combination of conventional catalysts and thin film catalysts as two model research objects may also lead to two distinct models that describe the data well but lack correspondence between limiting factors in both catalyst layers. This is to be determined.
- It is not clear how much of a variation the team will be able to produce in terms of agglomerate size and other parameters of interest in the experimental project.
- There is no clear link between model development and specific changes to traditional CCLs. The thin film catalyst is not performing well.
- The thin-catalyst-layer approach does not seem like a viable path to mitigating mass-transport limitations at HCDs.
- There is a lack of model validation using SOA catalysts and MEAs.

Recommendations for additions/deletions to project scope:

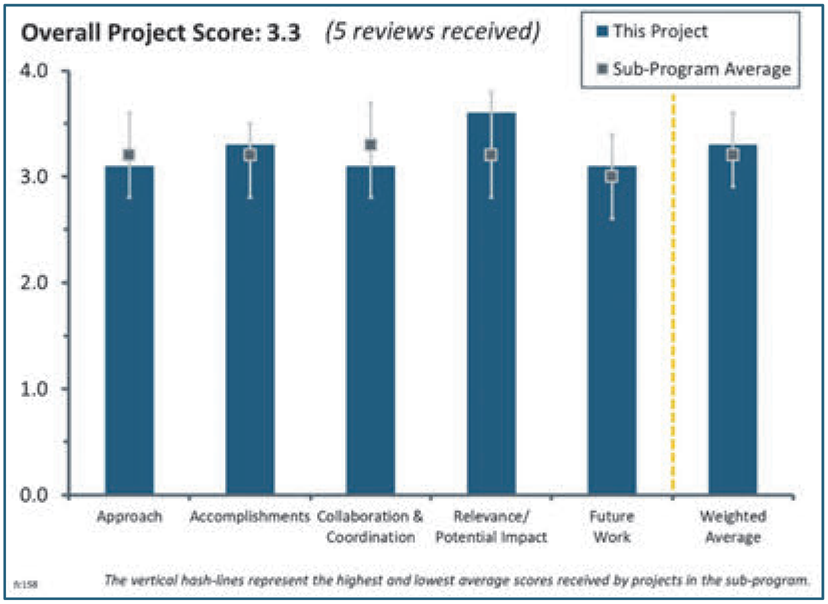
- Additional collaboration on the electrode characterization could be beneficial (using X-ray nano-CT, for example).
- It is recommended that the project use data from other groups with very different structures to test the model. Dropping the catalyst development work is also recommended.
- It is suggested that the project incorporate a new go/no-go point associated with the thin film catalysts to demonstrate acceptable cathode performance before any further development or model development.
- The electrochemical characterization and, in particular, the measurement of the limiting factor could be enhanced by the application of an impedance spectroscopy. This is to demonstrate resistance fingerprints in varying conditions, for example, in 100%, 20%, and 10% oxygen that has been diluted in nitrogen or helium (something like a half-helix). This step could further complement the model and show what key (experimental) measurable characteristics are indicative of the specific modeled issues in diffusion limitation.
- Regarding non-conventional catalysts and catalyst layer structures, the focus should be on the catalyst that has potential to get commercialized. Many efforts have been put into thin film Pt catalysts without much interest from industry. SOA catalysts, nanofiber electrode structures, or other new catalyst layer structures should be considered for validation.
- The deposition of thin Pt layers by sputtering should be deleted from the project scope. Electrodeposition is a more viable approach, as it provides much more flexibility compared to physical methods, in terms of microstructure control. This approach has been successfully demonstrated by Dr. Adzic’s group within the DOE-funded Hydrogen and Fuel Cells Program.

Project #FC-158: Fuel Cell Membrane Electrode Assemblies with Ultralow-Platinum Nanofiber Electrodes

Peter Pintauro; Vanderbilt University

Brief Summary of Project:

Particle/polymer nanofiber mat electrodes are a promising alternative to conventional fuel cell electrode structures. This project seeks to better understand and further improve the performance and durability of low-platinum-loaded nanofiber mat fuel cell electrodes and membrane electrode assemblies (MEAs). Mat electrode MEAs with highly active oxygen reduction reaction (ORR) catalysts for hydrogen–air fuel cells will be fabricated, characterized, and evaluated. The project will focus on nanofiber cathodes with commercial platinum–alloy catalysts and platinum–nickel octahedral catalysts containing various ionomer and blended polymer binders.



Question 1: Approach to performing the work

This project was rated **3.1** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The objectives of this Vanderbilt-led project are clearly defined, as are the barriers it aims to address. While not unique (electrospinning has become quite popular in energy research worldwide), the approach is viable and promising, especially following the recent introduction of a water-soluble binder.
- The approach is to tune the structure of the catalyst layer by shaping the conventional Pt/C and ionomer into nanofibers. The fiber approach to catalyst layer construction yields surprisingly excellent results. The partnership with the Georgia Institute of Technology (Georgia Tech) with new catalyst material appears to be a distraction from the overall project approach.
- The project attempts to improve high-current-density performance and durability using an alternative approach of coating the electrode with sub-micron-size fibers; the advantage of this approach is fundamentally unclear, as the structure is not maintained after MEA fabrication.
- The electrospun electrodes are showing early promising results. The unanswered question deals with why, and inherently why these electrodes would be expected to be an improvement over more conventionally supported catalysts that use the same Pt–alloy catalysts. Early characterization results are giving some clues, but more effort is needed here (and, to the team's credit, is listed in future work). The Fuel Cell Consortium for Performance and Durability (FC-PAD) is well suited to this task. A more systematic approach is necessary to understand the interaction between structure, materials, and conditions on performance (i.e., questioning how ionomer-to-carbon-weight ratios (I/C), porosity, ionomer, carrier choice, etc. affect polarization curves, stability/durability, loss contributions, etc.).
- The idea to use electrospun fibers in fuel cell catalyst layers is excellent. However, the materials could be characterized much better. Beyond a scanning transmission electron microscopy (STEM) micrograph, there was little information. The authors should characterize the pore size distribution with mercury and/or N_2 porosimetry. The performance of the fuel cell will be highly dependent on the pores available (water management), so their characterization in the catalyst layer, preferably with ionomer, is critical. The type of

gas diffusion media used will also play a critical role in water management, as well as compression. While the team might be making these considerations, none of this information is in the presentation. As presented, the results were highly empirical.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The excellent fuel cell performance of the nanostructure fibers speaks for itself. The project contains excellent results.
- The performance of the electrospun nanofiber MEAs, especially those from Gen 2, is impressive, either already reaching or closely approaching the set of go/no-go performance targets for December 2018. The high porosity of the fibers appears to benefit the mass transport of oxygen (with more than tenfold improvement versus the sprayed-electrode baseline), facilitating water management and ultimately helping MEA performance at high current densities. The replacement of polyacrylic acid with an easily removable blend of an ionomer and carrier has resulted in a noticeable gain in the performance of Gen 2 MEAs relative to Gen 1. This, in particular, makes the latest-generation electrodes perform better than Gen 1 at low relative humidity (RH). The observed variation in the activation losses with the three electrodes is puzzling. It is relatively significant, possibly obscuring the true values of other performance losses, especially those associated with the mass transport (slide 10). There has been little progress in the development of PtNi/C octahedra catalyst at Georgia Tech. Catalyst development is the weakest part of this otherwise very good project.
- There is very nice progress (>900 mW/cm^2, <40% loss after 30K load cycles) at this relatively early stage. This does appear to be at a relatively high cathode stoichiometry, so it would be good to see the performance under a more applicable stoich (1.5–2.0) at high current densities. The baseline (sprayed) performance is also sub-par. The performance should be compared to a better-optimized Pt-Co MEA from, for example, other DOE projects (both in and out of FC-PAD). It is recognized that the nanofiber MEA is likely not yet optimized, so improvements on this are expected as well. While the polarization loss plot (on slide 10) shows improvement over the baseline sprayed catalyst, it does oddly show higher mass transfer losses (lower RH plot). Perhaps this is a measurement artifact, but it should be investigated. The principal investigator (PI) noted a loss in performance (max power density) going from 0.2 to 0.1 mg/cm^2 *total* loading (906 W/cm^2 versus 809 W/cm^2). However, the cathode remained relatively constant (0.1 mg/cm^2 versus 0.09 mg/cm^2, perhaps within uncertainty of measurement). It is questionable whether that difference would be due to reduction from a thick (0.1 mg/cm^2) anode to a very thin (0.019 mg/cm^2) anode. The difference may have been due to either a poor anode or, more likely, sample variation. Thus it is recommended that the project continue with a relatively fixed anode loading (at either 0.05 mg/cm^2 or 0.025 mg/cm^2) and focus on the cathode, with multiple samples tested to comprehend variation.
- Progress is made toward DOE goals; however, this is done (as presented) via an empirical approach. There is more of a focus on materials discovery/patenting rather than understanding why the materials are performing well. The researchers could do a better job presenting the state-of-the-art by using a Gore standard, or data published by General Motors, for comparison. The sprayed standard has very poor performance versus the state of the art, making the Vanderbilt results look more favorable compared to DOE results. It is not clear why the PtNi electrocatalysts should perform better than the commercial PtCo.
- There is good improvement over the previous generation's process. However, because the performance of the baseline spray process is awfully poor, benchmarking the progress is impossible. Overall, the data quality is poor.

Question 3: Collaboration and coordination

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

- The collaboration with Nissan is excellent, and the collaboration with FC-PAD is also good.
- The team appears to be working well together, and all researchers contributed to the project.

- The integration with FC-PAD to characterize the MEA is appreciated. It is recommended that this, combined with a systematic variation of the MEA processing (I/C, ionomer, carrier, electrospinning process parameters, etc.), be the focus for the following year. Nissan should be capable of building and performance-testing the final MEAs. The performance of the baseline PtCo-sprayed catalyst is surprising; this suggests some extra effort is also warranted on ensuring that the final MEAs are optimized. The integration of Georgia Tech's shaped catalyst with the project's main focus (electrospun nanofibers) is not clear.
- The efforts at Vanderbilt and Nissan Technical Center North America seem to be well integrated and complementary, with the two teams collaborating effectively. The contribution of Georgia Tech is less evident, clearly because of problems with obtaining a competitive PtNi catalyst. Collaboration with FC-PAD laboratories (Oak Ridge National Laboratory, Lawrence Berkeley National Laboratory, Argonne National Laboratory, and Los Alamos National Laboratory) has been generally very good, helping with the characterization and performance verification of nanofiber electrodes.
- As the project is an FC-PAD member, it would be nice to see more leveraging of the national laboratories' capabilities, especially in the MEA evaluation, as the data quality is quite poor.

Question 4: Relevance/potential impact

This project was rated **3.6** for its relevance to/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.

- Durable, high power densities at low/ultralow-platinum-group-metal (PGM) loadings are the key enabler to automotive fuel cell commercialization. Both materials (i.e., catalyst and support) and an understanding of their interactions (FC-PAD) are fundamental to achieving this goal. This is the type of work we need.
- This project is very relevant to the DOE Hydrogen and Fuel Cells Program goals and objectives. It promises to be successful, and if so, its impact on MEA technology could be substantial.
- The project has the potential for a major impact on improving the commercial viability of fuel cell systems for automotive applications (i.e., the overall DOE objective).
- High-current-density performance and durability are very important.
- The team is working toward DOE goals but in an empirical fashion. It would be useful to have some insight into why the materials are performing well and what parameters effect improvements.

Question 5: Proposed future work

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

- The proposed future work ensures continuity of the research performed so far, with a focus on what it promises will be an incremental improvement in performance through process optimization and assessment of electrode durability using standard accelerated stress tests. The PI lists several questions to be answered in the remaining part of the project. These are all important questions that, if successfully addressed, could help advance the electrospinning technology for fuel cell MEAs.
- The planned future work is good, but a more cohesive approach providing answers to science questions would be better. Less focus on proving the DOE laboratory theory of oxygen resistance as a limiting factor in performance would be helpful. The team should focus more on gas diffusion media/water management. The use of alternative catalysts should be considered—without waiting for the Georgia Tech materials. The team should focus on using different ionomers; this is being discussed but not done. Also, the characterization of the pore size distribution in the catalyst layer is likely critical to better performance.
- The future work proposed on slide 19 is what is needed. Specific details, however, will require fleshing out. It is unclear what material and process parameters are going to be varied and which ones will be subject to the battery of tests and characterization available to the team. Some systematic characterization of the process variables is needed (I/C, etc.). Perhaps a design-of-experiments approach can be employed. Startup/warmup needs to be addressed. It would be good to know how the material performs at -30°C, 0°C, and 30°C; it is recommended that the project run the U.S. DRIVE Partnership Fuel Cell Technical Team robustness protocol.

- The proposed work should focus on scale-up, durability, and cost analysis of fiber fabrication. Some justification should be made for the manufacturing costs of the electrodes, since it most definitely will be higher than simply ink casting conventional Pt/C.
- It would be nice to see more progress in integrating high-activity catalysts.

Project strengths:

- This is a well-designed project targeting enhancements in the MEA performance via the electrospinning of porous nanofibrous catalysts and ionomers. This progress has been excellent in the past 12 months, with project targets likely to be reached, and possibly exceeded, by the project end, if not earlier.
- The electrospun fibers are very interesting and hold much promise. This might also be interesting for liquid fuel cells that require higher porosity in the catalyst layer. The team is good and holds potential for more in-depth studies.
- The team has developed an electrode/MEA exhibiting early promising performance. The FC-PAD team brings a wealth of analytic and diagnostic capability, which is well suited to the project approach.
- The project could have an obviously big impact in power density and Pt utilization targets.

Project weaknesses:

- No weaknesses come to mind.
- There are not too many weaknesses in this project, except for the questionable value of the PtNi controlled-shape catalyst research at Georgia Tech.
- There is no clear weakness, although it is unclear how the Georgia Tech shaped catalysts integrate with the bulk of the project.
- The materials are poorly characterized. The electrochemistry at Nissan is focusing on answering issues of ionic and oxygen transport, with little emphasis on water management. There is no discussion of ionomers, gas diffusion media, or the role of MEA compression on cell performance. The project could likely hit DOE goals easily if the team would focus on the water management areas (i.e., gas diffusion and compression). The researchers should provide more technical insight into the pore size distribution in their electrospun fibers.

Recommendations for additions/deletions to project scope:

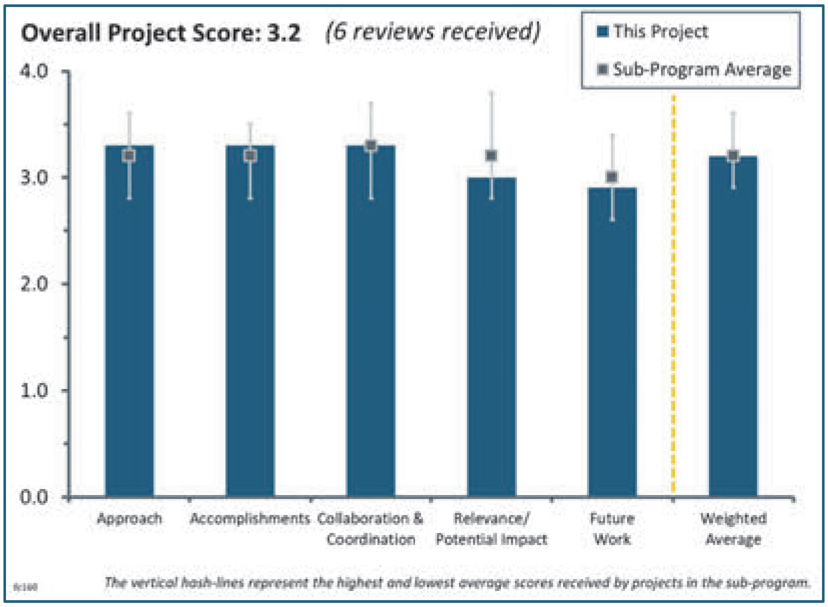
- The viability of PtNi shape-controlled catalysts from Georgia Tech should be verified, and if there is doubt, the resources should be reallocated elsewhere within the project. A considerable part of this research should focus on the impact of electrospinning on electrode durability and understanding the origins of the benefits rendered by the electrospinning of electrodes. The latter task will require correlating fuel cell performance and the comprehensive characterization of the electrodes and MEAs (likely to be provided by the FC-PAD laboratories).
- A de-focus on the Georgia Tech shaped catalysts is recommended. It is suggested the team increase focus on systematic parameterization (perhaps using a design of experiment) and optimization of the process variables (such as I/C, percentage of PGM, electrode thickness, ionomer, carrier, electrospinning process variables, etc.), complete with characterization and testing. It is also recommended the team include multiple samples where needed.
- The elimination of catalyst work at Georgia Tech is recommended—fibers need to be better characterized before the role of alternative catalysts can be understood.
- A cost analysis of manufacturing electrodes is necessary. Durability and drive-cycle operational stability should still be addressed.

Project #FC-160: ElectroCat (Electrocatalysis Consortium)

Deborah Myers (Argonne National Laboratory) and Piotr Zelenay (Los Alamos National Laboratory); Los Alamos National Laboratory

Brief Summary of Project:

ElectroCat (the (Electrocatalysis Consortium) was created as part of the Energy Materials Network in February 2016. The goal of the consortium is to accelerate the deployment of fuel cell systems by eliminating the use of platinum-group-metal (PGM) catalysts. ElectroCat and its member laboratories—Argonne National Laboratory, Los Alamos National Laboratory, National Renewable Energy Laboratory, and Oak Ridge National Laboratory—will develop and implement PGM-free catalysts and electrodes by streamlining access to unique synthesis and characterization tools across national laboratories, developing missing strategic capabilities, and curating a public database of information.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The team has developed an excellent approach to the work, proceeding to answer key questions in the development of PGM-free catalysts in a very structured and systematic way: by measuring key parameters in the catalyst, developing measurement techniques, and establishing process–composition–activity relationships. The high-throughput synthesis, characterization, and performance evaluation work has provided an effective way to develop relationships between catalyst composition and processing variables, with resulting catalyst properties. X-ray computed tomography (CT) work appears effective at increasing the understanding of the catalyst layer structure. The automated dispensing of inks and the fabricated electrode with a catalyst/ionomer gradient over the length is an effective way to provide repeatable fabrication and to understand ionomer composition effects. Modeling work is necessary and provides useful insight into active sites and linkages with electrode design. The approaches to begin the molecular probe of durability are good.
- The project approach is excellent, encompassing the full array of materials development, state-of-the-art characterization, and modeling capabilities that are available within ElectroCat. These capabilities are appropriately applied toward developing understanding and resolving the key challenges of non-PGM oxygen reduction reaction catalysts.
- This project has a very good combination of materials discovery and tool development. It would be good if the project explained the difference between ElectroCat (a consortium of national laboratories) work and funded project work.
- This project partners with very strong leaders from four national laboratories, each with proven capabilities and expertise in the key technologies that are critically important for project success.
- This consortium is advancing state-of-the-art catalysts for PGM-free fuel cells, developing new tools, and improving understanding of the catalysts. A minor shortcoming is the narrow focus on mainly an Fe-N-C

catalyst that may possibly be inherently unstable, but at this point, no other PGM-free catalyst is competitive.
- Extensive ex situ and in situ characterization of PGM-free catalysts was done. However, the focus is primarily on Fe-N-C, and therefore, the ultimate usefulness of this work will be limited. The high-throughput addresses only a narrow range of parameters that are expected to give only incremental improvements. Stability is not a criterion in high-throughput screening; it is hard to see any innovative approach that will significantly improve the volumetric activity and stability.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team has made good progress and has exceeded a key milestone. Excellent progress has been achieved in a number of areas: the correlation between composition and activity, the development of molecular probes, the characterization of important processes and composition variables, and the development of a repeatable fabrication process and further developed models.
- The project has made excellent progress across multiple fronts, including furthering understanding of the active sites and, more importantly, degradation of the active sites and resultant performance loss. The team is making excellent use of several advanced characterization methods toward this effort.
- A method for estimating the demonstrated active site density will help with understanding and improving the active site structure. NO_2- was successfully used as a molecular probe, but the catalyst will also have a nitrogen species, so it is uncertain if this is a Fe-N species interaction with a probe molecule.
- The active site probe work is a major accomplishment in this field. The durability characterization work was very enlightening.
- This project team has shown significant and continuous progress in each of the four key areas of development: catalyst development, electrode and membrane electrode assembly (MEA) development, high-throughput fabrication, and modeling. The lead investigators have placed each of these areas under the leadership of proven organizations that are consistently meeting their interim targets. Progress is approaching the project goals. One area that requires additional focused attention is the migration of Fe. While this report shows Fe migration through the catalyst layer away from the membrane, the test time is extremely short, and many operating modes still need to be tested. To the extent that Fe reaches the membrane in any of the operating modes, the resulting Fenton reaction will severely limit the membrane durability. Since this project introduces Fe into the catalyst, it must define a solution path.
- The molecular probe to determine the active site/site density is interesting. There should be a paper study to estimate what is needed for this catalyst family to be practically useful. The primary focus is on initial performance. It would be interesting to benchmark the materials against a state-of-the-art PGM catalyst on performance and durability to understand the status, and justify if there is any tangible progress. Each year, progress should be benchmarked against a state-of-the-art PGM catalyst at relevant operating conditions (air, Q/dT).

Question 3: Collaboration and coordination

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

- The collaboration across all ElectroCat members is clear and directly relevant toward achieving desired project outcomes.
- There is excellent coordination between partnering laboratories for material and tool development.
- Work appears to be well coordinated, cohesive, and comprehensive.
- This project has plenty of collaboration. A minor concern is the lack of original equipment manufacturer collaboration.
- This project contains very close collaboration between national laboratories. The lack of partnership with any major industrial players begs many questions. The relevance and impact of the project are likely small.

Question 4: Relevance/potential impact

This project was rated **3.0** for its relevance to/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.

- Fuel cell stack cost is still one of the main challenges in DOE's Fuel Cell R&D sub-program. Eliminating PGM completely will definitely help meet the material cost target, but performance and durability targets for transportation application will be challenging to meet. A combination of very low-PGM (i.e., 1% or 2%) and highly active PGM-free catalysts may be able to meet the cost and performance targets. If DOE agrees, this should be explored as one of the options at the end of the project. The main focus should be on PGM-free catalyst development.
- The PGM catalyst is projected to be the most expensive single contribution to the cost of the fuel cell stack. Eliminating the PGM while maintaining the current level of specific power, power density, peak energy efficiency, and durability will significantly accelerate the deployment of fuel cell systems.
- The project is relevant to long-term goals for lowering fuel cell cost. An immediate commercial impact is not likely.
- The project is well aligned to address the key cost, performance, and durability barriers that are slowing commercialization of fuel cell technology. One area of concern is that the relatively large effort within the Fuel Cell Technologies Office for PGM-free catalyst development may not ultimately result in commercial fuel cells, and if it does, the timeframe may be measured in decades. The PGM-free field has made excellent progress in improving the activity and performance over the past decade (further gains are still needed), but the significant durability and performance degradation issues that are evident over periods of tens of hours (vs. 5000- to 8000-hour targets for fuel cell electric vehicles) under rather benign conditions are extraordinarily concerning. Real systems will spend considerable periods of time at relatively high potentials (e.g., >0.7 V) and have start–stop events, the latter of which is the elephant in the room (i.e., carbon corrosion stability). The project is performing the right type of work to understand the durability, but a key question is whether this class of catalysts will ever be sufficiently durable for commercial applications—this should be assessed as soon as possible. Recently, PGM-based catalysts, supports, and electrodes have rapidly been achieving DOE performance targets, and an additional loading reduction factor of 2 may substantially address most of the remaining gap for achieving the ultimate target of $30/kW. The questions/concerns around PGM-free catalysts are not reflective of the high quality and excellent research being conducted in the project, but should be addressed to understand the relative priority of this class of materials with relatively longer timeframes for potential commercialization.
- The work from this project is highly valuable and of high relevance for the development of PGM-free catalysts. While much progress has been made, the path of these catalysts to high-power density and long durability is still uncertain, which may limit applicability.
- Reducing the amount of PGM is important, but the impact of a PGM-free catalyst on cost is overstated. The use of iron and the low stability of the catalyst must be addressed.

Question 5: Proposed future work

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

- The future work is appropriate. It is recommended that the project increase work on understanding the electrode design and increase efforts on understanding the degradation mechanism.
- This consortium is making good progress, and no major changes are needed. Some expansion of the types of catalysts that are being analyzed would be beneficial.
- Overall, the proposed future work is good, continuing fundamental studies across the breadth of topics necessary to advance the PGM-free activity class. Additional near-term work should assess carbon corrosion stability, one of the primary (and perhaps fundamental) barriers with carbon-based non-PGM catalysts.
- Short-term durability testing has identified some potential issues. Longer-term testing, as well as a broader test base, is necessary. The potential risk with Fe is high, and so a solution path is needed. The larger MEA area has to be demonstrated.

- The project's proposed future work consists of continuing development on Fe-based catalysts, which attract little interest from industry. There is a large amount of work in the study of performance and stability of a catalyst family that might not be relevant.
- More efforts on MEA optimization would be needed.

Project strengths:

- The project's strengths lie in a comprehensive and cohesive effort to systematically study catalyst composition and processing parameters' correlations with catalyst activity. Strong characterization tools are incorporated, and the modeling approach is informing the work. This is an excellent team.
- The project team consists of leading experts in the PGM-free catalyst field and includes expertise in PGM-free catalyst design, synthesis, and characterization. The project has access to the necessary state-of-the-art characterization methodologies needed to make rapid progress.
- This project is advancing catalyst performance, test/analysis capabilities, and fundamental understanding in the field of PGM-free catalysts.
- This project group is very experienced, as shown by the members' previous work. The lead investigators and their partners are capable of successfully completing this program.
- This is a team of expert researchers and tool developers.

Project weaknesses:

- No real weakness was identified.
- The primary project weakness is that the durability of PGM-free catalysts may not be addressable, which would significantly limit the utility of this technology commercially within the next decade(s). Carbon corrosion stability may be a likely key fundamental barrier, which should be assessed in the nearer term.
- Current Pt anode loading in an MEA is still higher than in a PGM MEA. Lower anode loadings should be explored. It is safe to assume there is no effect of anode loadings, but, to avoid any surprises, anode loadings should be lowered at an early stage of the project.
- A materials and capability development investment of $4M/year is quite large, considering the relevant output from the project. There is a negligible interest from major industry players.
- This project needs to develop a solution path to verify that Fe will not leach out of the catalyst layer over time, at all operating conditions that can be anticipated.
- The project is focusing on Fe-N-C catalysts that seem to have inherent durability limitations.

Recommendations for additions/deletions to project scope:

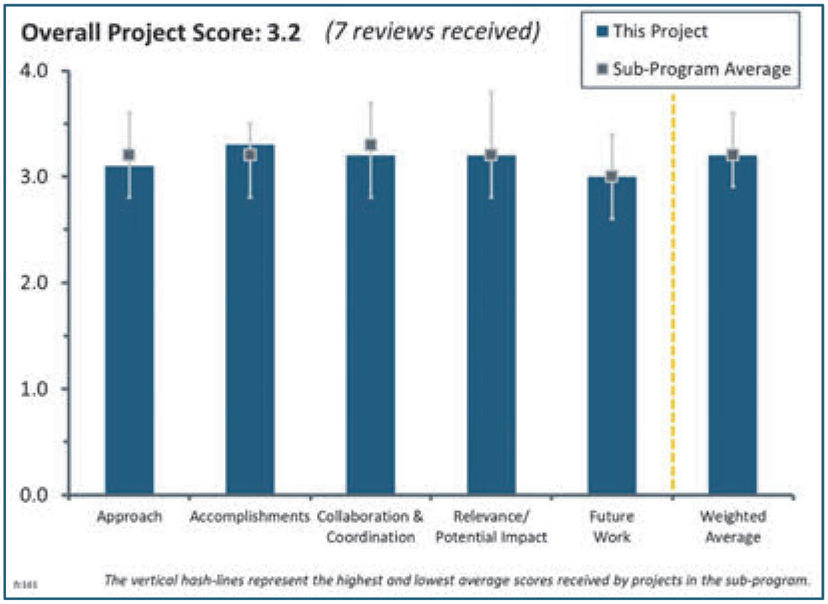
- It is recommended that the project increase efforts on modeling the electrode structure and aligning a "possible" future catalyst design with an optimized model design. For example, it is suggested that the project take into account the realistic concentration of achievable active sites, electrode thickness, and transport effects. Efforts should be increased to understand the degradation mechanisms.
- Some expansion on the types of catalysts that are being analyzed would be beneficial (i.e., other metals, non-metal, polymeric, other carbon dopants, etc.).
- A combination of low PGM (1%–2%) and the best of PGM-free catalysts should be explored as an option in case PGM-free catalysts do not meet performance targets.
- The project should dramatically increase focus on addressing durability. Activity and performance at beginning of life is approaching Pt electrodes (within a factor of 2), but durability is the key barrier.

Project #FC-161: Advanced Electrocatalysts through Crystallographic Enhancement

Jacob Spendelow; Los Alamos National Laboratory

Brief Summary of Project:

Los Alamos National Laboratory (LANL) seeks to design active and durable oxygen reduction reaction (ORR) catalysts based on fully ordered intermetallic alloys on highly graphitized nitrogen-doped carbon supports and demonstrate them in high-performance membrane electrode assemblies (MEAs). Synthetic work is guided by computational ORR kinetic studies, and each round of synthetic development is further guided by feedback from MEA testing and characterization studies.



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 identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- Atomic-level ordering is a very good approach for durable catalysts; the project has several catalyst candidates that were developed simultaneously.
- The approach of this project is in agreement with other similar projects that are aimed to address the U.S. Department of Energy technical targets for Pt-based systems.
- The multiple approaches for risk mitigation and technique comparison are good. This is a good team that is clearly working together. The support work seems less valuable than catalytic development. There is concern that the support work will divert effort away from the strong catalytic developments.
- This project utilizes a wide pool of characterization techniques, as well as computational tools, to guide the design and synthesis. Different synthesis techniques and processing methods have been employed to achieve atomic-level ordering to increase performance and durability of Pt-based catalysts.
- The proposed approach is addressing the project goals. The only minor concern is with the project design, as it is not clear how the efforts of the catalyst synthesis collaborators are related, or beneficial, to one another.
- The approach is based on the hypothesis that the intermetallic alloy structure will enhance activity and stability. The idea has been tried many times without sufficient execution. Therefore, the risk is somewhat high. The project employs several approaches to prepare the structure, and hopefully some approach(es) work. The team evaluates MEAs for performance.
- While some catalysts in this project have shown promising mass activity, they all show quite low electrochemical surface area (ECSA). The participants need to clearly demonstrate that they have a path to achieve performance targets at >1.5 A/cm^2. This could be by increasing ECSA, increasing mass activity, or reducing local oxygen transport losses. Regardless of the approach, there is currently no clear evidence that this will be achieved.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Thus far, there has been excellent progress from a fundamental aspect in regard to characterization and evaluation.
- The team has met some difficult targets this year. The team showed some characterization results supporting the importance of the ordered structure. The presentation of the data is clear and fair.
- The project is on track and is focused on achieving DOE goals for cathode catalysts.
- The project is clearly laid out; clear and significant progress has been achieved.
- Progress has been made in the synthesis and characterization of intermetallic Pt alloys with transition metals. However, the idea and execution cannot be entirely associated with this project, considering that identical systems have been proposed and reported before. Nanoparticles presented cannot be referred to as high-quality materials. The main focus in this project is to induce control of the structure; nevertheless, transmission electron microscopy (TEM) micrographs, X-ray diffraction patterns, and cyclic voltammetry (CV) do not indicate a high level of ordering. Instead, that is likely to be random effect. Moreover, particle size distribution is significant, including size and irregular shape. On the other hand, the measured performance of the MEA did exceed the DOE technical targets.
- The team shows promising results for certain metrics or catalysts, yet scale-up needs to be demonstrated. Results on structural changes upon accelerated stress tests (AST) are interesting and useful for understanding the key phenomena. Advanced characterization studies nicely complement the data from MEA testing.
- While some of these catalysts show decent mass activities, their relatively low ECSA is a concern. Only the LANL face-centered-tetragonal (fct)-CoPt appears to have an ECSA approaching a value close to what will be required for automotive applications. If the principal investigators believe this problem can be overcome through reducing local transport losses, they should provide evidence/modeling to show what combination of ECSA, mass activity, and local transport losses will be required.

Question 3: Collaboration and coordination

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

- There has been excellent collaboration among the team members, which is evident from results.
- This multi-method approach helps the industry as a whole by focusing on what methods are best for these catalysts.
- The team has good collaboration and coordination, especially on synthesis of catalyst structures and their characterization and testing.
- Collaborator roles are clearly delineated.
- All project partners appear to be engaged.
- While the project has collaborators, it seems there are three parallel projects being pursued.
- The team uses national laboratories' capabilities well. Results from sub-contractor universities are fewer. Participation from EWII Fuel Cells was not evident.
- It is unclear how the result of this work will be transferred to the market. There was no talk with a major industrial player. The precious metal market is very competitive, and it is unlikely that a new small player can profitably compete. It is debatable whether materials development at this level is appropriate at a national laboratory.

Question 4: Relevance/potential impact

This project was rated **3.2** for its relevance to/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.

- The project's scope and goals align well with the DOE objectives on improving catalyst performance and durability for fuel cells.
- This project is addressing DOE targets and, if successful, will be impactful with regard to reducing fuel cell cost.
- This project is relevant to DOE's fuel cell research and development roadmap to meet DOE's 2020 target.
- Durable high-activity catalyst development is important.
- This is very relevant work. One limiting factor is perhaps the high amounts of transition metals that are currently being used. It is unclear whether there is a plan to reduce the amount of cobalt.
- The modeling work is of value. However, until clear evidence of or a plan for how high current density performance will be achieved is presented, it is unclear how impactful the work will be.
- The potential impact of this work cannot be seen as high, considering that other programs have proposed and made identical systems.

Question 5: Proposed future work

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

- The future work plans are well described and are in line with the overall project goals.
- The project is on track, and the proposed future work is the logical next step. A minor potential issue is that the catalyst down-select process to identify "promising catalysts" was vague. No technical targets were given for what catalysts must achieve to be down-selected.
- Scale-up and integration work is certainly of importance. However, as mentioned, some modeling effort to demonstrate that the partners have a viable approach to achieving high current density performance is required (although the modeling effort does not have to be extensive).
- The high content of transition metals should be addressed. Additional modes of operation may cause significant decay and cobalt leaching.
- Future work is a logical continuation of this effort, which is supposed to address challenging steps such as scaling up and characterizing 50 cm^2 MEAs.
- Down-selection of a promising catalyst is mentioned in the future work, so it is expected that the team will do this earlier rather than later so efforts can be focused on the best catalyst.
- It is unclear what the down-selection criteria are and whether there is a go/no-go decision point for unproductive approaches/partners.

Project strengths:

- The team's approach with different synthesis methods guided and supported by various testing and characterization is a strength. The project partners, a decent set of publications, and presentations were also project strengths.
- Modeling appears to be providing useful guidance for catalyst synthesis. Several catalysts with promising mass activities have been prepared.
- A project strength is the strategy to work with well-controlled Pt alloy nanoparticles, well-executed electrochemical performance in MEAs, and careful TEM studies.
- National laboratory and university collaboration is strong. Exploring new ideas such as the hydrogel approach is also a strength.
- This is a good approach. The team has shown solid work, strong results, and good collaboration.
- LANL is developing alloy catalysts that so far show promising activity and stability.

Project weaknesses:

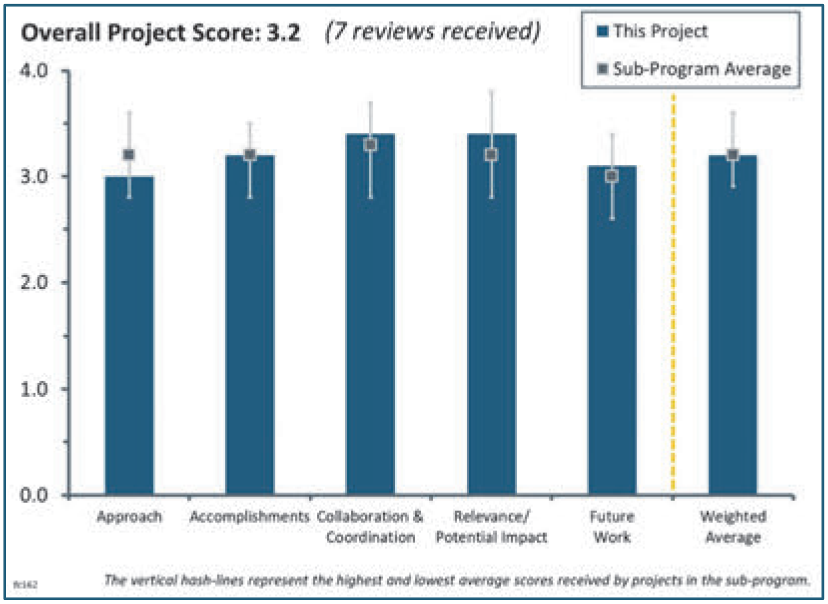
- The path to achieve high current density performance is rather ambiguous and seems to rely on anticipated advances in ionomer or other methods to reduce local oxygen transport.
- High activity has been achieved, but with high transition metal content. N-doped carbon supports distract from the core catalyst work.
- There are no specific project weaknesses, although scalability is an overall concern.
- Multiple synthesis routes are being pursued, but it is not clear how these routes are complementary.
- The outcomes would be identical to those other programs have already achieved.

Recommendations for additions/deletions to project scope:

- The team should eliminate carbon support development and perhaps attempt to deposit the catalyst on more existing types of supports for comparison.
- To fully utilize the team’s potential, the lead researchers should focus on systems that are unique to this project.
- It is recommended that LANL down-select the two best catalysts and focus the electrode work. Otherwise, the experimental matrix may become too large.
- The team should immediately add a strong focus on how to achieve high current density performance.

Project #FC-162: Vapor Deposition Process for Engineering of Dispersed Polymer Electrolyte Membrane Fuel Cell Oxygen Reduction Reaction Pt/NbO$_x$/C Catalysts

Jim Waldecker; Ford Motor Company



Brief Summary of Project:

The objective of this project is to develop, integrate, and validate a new cathode catalyst material by developing and optimizing a vacuum powder coating physical vapor deposition (PVD) process. Project tasks include (1) development of a new cathode catalyst powder made of titanium, niobium oxide, and carbon; (2) improvement of the PVD process for the manufacture of the catalyst powder; (3) cost-effective scale-up of the PVD process; and (4) integration of the developed cathode catalyst powder into established fuel cell manufacturing processes.

Question 1: Approach to performing the work

This project was rated **3.0** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project team, led by Dr. Waldecker, will address the main issues with fuel cells for the automobile industry to produce a high-performing membrane electrode assembly (MEA) at rated power (with the U.S. Department of Energy's recommended Pt loading), while the electrocatalyst allows an increase in durability to the targets described in the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan (MYRDDP). The relevance, targets, and proposed work were clearly presented in the slides and were described during the review. The team, under the supervision of Ford Motor Company (Ford), will explore design, synthesis, evaluation, and scale-up of a Pt-NbO$_x$/C catalyst, which will be integrated into the catalyst layer of the electrode. The main challenge of these materials is the low reproducibility of almost all synthetic approaches (which the team has already experienced); however, the well-known synthetic expertise of Exothermics, Inc. (Exothermics) and Oak Ridge National Laboratory (ORNL), in combination with the leader of MEA fabrication, EWII Fuel Cells, will no doubt make the project feasible. It should be mentioned that the principal investigator (PI) spent enough time during the beginning of the presentation explaining to the audience all key aspects of the project, the role of team members, and challenges faced. The team leader also gave a full picture of the technology and explained the logic behind the selected tasks for budget periods I and II, as well as the milestones.
- The PVD approach to make catalysts using direct Pt deposition onto the support material is a good way to eliminate the complexity of a wet catalyst synthesis process. 3M practices a similar vacuum-assisted sputtering process to deposit Pt on carbon whiskers to make 3M's nanostructured thin film catalyst. The approach is viable and has all the advantages cited by the PI in this presentation on slides 5–7. The simplicity of the PVD process is expected to make it cost-effective. However, the team may need to fine-tune their cost estimate as shown on slide 7. The processing cost estimate by Exothermics may be early, and going forward, the team needs to validate the estimate. Since the team is not going to anneal PVD-made catalysts, their stability under ink-making conditions (such as ultrasonication, homogenizer, etc.) needs to be evaluated by the team.

- The overall approach of using niobia to try to stabilize Pt offers some potential advantages. The approach of preparing catalyst powder samples using PVD is unique and has potential for a lower-cost catalyst-preparation method. The work has been focused on meeting the activity milestone and not on demonstrating a key hypothesis and differentiating factor for this project (i.e., the hypothesis that niobia improves Pt durability). The work should have more focus on addressing whether niobia improves durability. The approach to date has lacked focus on characterization and on understanding what is happening in the system. Characterization of the samples has been lacking. The project to date does not appear to have effort directed toward determining how much of the carbon is covered by niobia, or the niobia particle size. These are expected to be key parameters, considering the hypothesis put forth that the niobia helps pin the Pt particles. If the goal is for niobia to improve Pt durability, it is not clear how the very low (some less than 0.2%) niobia loading will contribute.
- The approach is clear and proceeds logically. The approach thus far has not focused on durability, which will be critical in establishing the benefit of Nb, but this is to be addressed in the coming period. Of particular interest is whether the relatively low Nb composition examined would be enough to improve durability, or whether the performance would suffer if a higher Nb composition were needed.
- The PVD method indeed has great potential, but the specific advantages over other methods have not been highlighted sufficiently (for example, the control over oxygen stoichiometry NbO_x).
- The project team is working on simplifying a PVD process for improved reproducibility. However, to date, the PVD process appears to have issues with "line of sight," and getting uniform niobia does not appear to have happened. There are issues with reproducibility between the two systems in use; either this needs to be fixed, or one of the systems needs to be discontinued. At least from the discussion, it seems the tumbling of the carbon is not yet as reproducible as it needs to be. The team has shown various loadings of niobia on carbons; however, the weight percent of NbO_x has been relatively low—samples range from 0.5% to 13.3% (on slide 12), and slide 5 shows a 17.6 wt.% NbO_x sample. However, it seems unreasonable that a full coverage on the acetylene black can be obtained at any of these weight percentages. Noting that, of course NbO_2 is six times heavier than carbon, and these carbon materials are rather porous.
- The effect of Nb on the catalysts is not very clearly illustrated, nor is the parameter space. It is unclear what the catalyst parameters to be varied are.

Question 2: Accomplishments and progress

This project was rated **3.2** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The presentation was very well made by the PI. All the information provided in the presentation was very specific and clear. The charts were easy to read and understand. The team has made excellent progress in the last year. The project has accomplished both small- and large-batch catalyst synthesis at Ford, ORNL, and Exothermics and then characterized the catalysts at the University of Michigan and Northeastern University. The team has also prepared ink using PVD-made catalysts, prepared catalyst-coated membranes (CCMs), and assembled/tested them under polymer electrolyte membrane fuel cell conditions. Some of the team's accomplishments are commendable:
    - The discovery and validation of the use of two targets to achieve higher electrochemical surface area (ECSA) for the catalysts
    - The use of a Ketjenblack carbon black support to achieve a higher catalyst surface area and activity for large-scale production conditions
    - The discovery of the lack of effective Pt-Nb alloying in small-batch catalysts and a small amount of alloying for large-production batch catalysts

  Overall, the project team has had great accomplishments. The team was able to demonstrate a high-performing MEA made using a production lot catalyst from Exothermics (#Exo-180308, on slide 19) with a mass activity of 352 A/gm_{Pt}. Although this mass activity does not meet the DOE's 2020 target, it is nonetheless close.
- The project team demonstrated outstanding progress toward the project's final goal; all interim milestones were passed, and a quite challenging (for a new material class) go/no-go performance was obtained at two testing facilities. Taking into account a number of synthetic difficulties the team had at the beginning of the project, and how quickly they were addressed, the team has a perfect trajectory toward budget period II. All

milestones and go/no-go targets were based on measurable characteristics, either the materials (physical/chemical) or the final fuel cell performance of Pt-NbO_x/C electrodes, which fully complies with the DOE requirements and allows for a clear estimate of project success.

- The project has meet its Year 1 go/no-go milestone. The project has obtained good activity for a Pt/C catalyst and has been able to improve that activity with an alloy catalyst. Efforts have been focused on obtaining the activity milestone, and the characterization of the samples has been lagging (e.g., the particle size of niobia deposited is not known, Pt location relative to niobia is not known, and ionomer location relative to Pt and niobia is not known). The deposition techniques have not been able to deposit a narrow size distribution of Pt particles. This results in large particles that have poor Pt utilization and small Pt particles that offer high initial catalyst activity and high Pt utilization but are more susceptible to dissolution and have poor durability. The large particle size distribution may make it difficult to achieve the durability and activity targets simultaneously, as the smaller particles needed to make up for the lower mass activity of the large particles are inherently less durable. The inability to produce a smaller particle size distribution could potentially be what limits this approach. The project has had some difficulty in creating alloys, and Co has been formed as an oxide, rather than being incorporated into an alloy, decreasing the benefit of the alloying element and increasing durability concerns.
- A variety of batches have met the DOE performance target in Milestone 3. The large-scale batches are also promising and do not show a loss in performance with scale. There are some questions with respect to why the specific activity varies between sample sets. Some alloying was observed in the PtCo materials but not in Pt-Nb. The PtCo/NbO_x/C specific activities, however, fall within the range of Pt/NbO_x/C values. It is unclear whether alloying has had an effect on performance and what route would further improve activity.
- The durability has not yet been assessed, even though it is a key driver for this research; however, it was stated during the presentation that milestones have been moved forward.
- The project has made progress to date by producing a series of samples to demonstrate the process. The process details still need some improvement, as evidenced by the clustering of particles and sparse areas. The post-characterization is rather valuable, including x-ray photoelectron spectroscopy (XPS), ECSA, and mass activity; more needs to be done. The project has shown mass activities that are quite reasonable, as are ECSAs. However, it is unclear what the role of the NbO_x is; on slide 16, the NbO_x weight percent is only roughly 0.2% to 1.5%. It is likely the team could have obtained the same ECSAs with 0% NbO_x, and possibly the same mass activities. At these low concentrations of NbO_x (even 1.5%, which is still roughly 6% NbO_x by weight, with reference to the carbon material), it seems likely the vast majority of the Pt is deposited onto the carbon support. Slide 17 has higher concentrations of NbO_x; however, no strong correlation between NbO_x percentage and mass activity or ECSA is clear. Thus, in the end, more work is needed to understand the NbO_x coverage and the role it plays in the results.
- Clear progress toward meaningful milestones is made, even if the trends, and an understanding of why this is happening, are not there. There seem to be too many variables to down-select; a focus on one source of PVD is suggested. The use of better proven carbon supports is also suggested.

Question 3: Collaboration and coordination

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

- The team is composed of very experienced and reputable scientists from academia and industry. Ford and ORNL are very well versed in DOE projects, and the PI, Jim Waldecker, is very experienced in running such projects. The academic, national laboratory, and industry combination of the team is adequate to successfully drive this project.
- The impressive overcoming of initial irreproducibility in catalyst composition is a solid indication of effective team work. All partners participated in the reviewed budget period and contributed to demonstrated accomplishments.
- The project has a good set of partners, and materials are moving between them. Northeastern University and ORNL may stand the best chance at understanding the fundamental interaction between Pt, NbO_x, and carbon.
- The collaborators and roles are clearly presented, along with which partners contributed to each milestone. There are a number of institutions being coordinated in this project, and each provides value.

- Collaborations between Ford, EWII Fuel Cells, ORNL, and Exothermics appear to be going well so far. Collaborations with the National Renewable Energy Laboratory and the Fuel Cell Consortium for Performance and Durability appear to be just getting started.
- There appears to be excellent collaboration in view of meeting milestones, with a shared common sense of urgency.
- The collaboration seems very good, with multiple exchanges and interactions demonstrated.

Question 4: Relevance/potential impact

This project was rated **3.4** for its relevance to/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.

- The project is very relevant to the MYRDDP. The proposed PVD catalyst development goals are aligned with DOE’s 2020 performance targets for electrocatalysts and MEAs for transportation application. The project team’s development of a large-scale manufacturing process at Exothermics is expected to meet DOE’s cost-effective and high-yield catalyst manufacturing strategy.
- Low-platinum-group-metal with high-platinum-mass-activity stabilized platinum particles for increased durability is a highly relevant area. These types of projects are a major cornerstone of the DOE Hydrogen and Fuel Cells Program (the Program), which could have an impact on the next generation of fuel cell vehicles. This project is exploring a new cathode catalyst powder that has the potential to stabilize platinum particles and reduce carbon corrosion.
- The accomplishment of all technical targets will provide a substantial support to the Program’s goals and objectives, especially taking into account that, according to a tech-to-market analysis, the catalyst will be cheaper at scale, with a tremendous potential for higher durability.
- The project addresses catalyst activity, cost, and durability. It supports and advances the Program’s goals and objectives.
- The project is relevant and addresses both the cost and durability barriers. The project supports DOE goals and objectives.
- The true benefit of the NbO_x has yet to be demonstrated during the cycling testing. To enhance performance, there is a benefit to the alloy catalyst PtCo, but this (which is already proven) is not the scope of the project. There could be a significant effect on catalysis with support/spillover onto NbO_x.
- While Nb is supposed to help with Pt stability, support stability is not addressed. A shift to better-performing supports should be planned.

Question 5: Proposed future work

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

- Future plans will be mainly targeted to address durability issues and improving MEA performance. The stability and durability protocols recommended by the FCTO (in the MYRDDP) will be used, and the beginning-of-life (BOL)/end-of-life parameters will be benchmarked with previously tested commercial Pt/C catalysts. The detailed characterization planned will build a correlation between the structure of the catalyst and its performance, accelerating the achievement of the final project goal.
- The proposed future work is logical and relevant. The added milestones to address durability are an improvement in the work plan. The planned increased effort in characterization is also appreciated. The proposed future work does not appear to include any effort to narrow the platinum particle size distribution, which is considered a key factor in obtaining both high activity and high durability.
- The proposed future work addresses most barriers; specifically, there will be a focus on durability and materials characterization. Work at high current density may also improve performance at rated power.
- The team clearly understands the shortcomings of the work so far and is planning to address them.
- The team has correctly identified the scope of future work and documented it on slide 24. Durability and mass-transport loss are two of the vital pieces of information needed to determine the feasibility of using PVD-mediated oxygen reduction catalysts in fuel cells. Since the PVD-made catalysts have less alloying,

their stability/durability under start/stop and load/humidity cycling is vital to the success of these catalysts. The start/stop and load/humidity cycling tests should be part of the future work.
- It seems that producing the anticipated materials has been more difficult than expected, hence the backward shift in the testing phase of durability testing. The planned structure is good, but there could be time limitations in having a feedback loop generate incremental improvements in catalyst design.
- All durability measurements are included in future work—this is critical for the success of the project. An understanding of the Pt/NbO_2/C structure to the appropriate detail is missing in the proposed future work section. The coverage of NbO_x on the carbon is unknown, as is how much of the Pt is on the NbO_x and on the carbon, respectively. It is unclear how the carbon pores are affected and how much of the results are due to Pt/NbO_x interactions and to Pt/C, respectively. There is much fundamental understanding of this system that is not being addressed in the future work. These details will help other projects in the future.

Project strengths:

- In terms of technology, the sputtering technology can create unique catalyst structures cost-effectively. The PVD method is being practiced today by many commercial electrode manufacturers. The team has demonstrated the method's feasibility in small- and large-scale methods. The approach of making a single-layer catalyst by sputtering is expected to be more cost-effective than the layer-by-layer sputtering approach. The possibility of efficient recyclability by the PVD process is another strength of the project, as depicted on slide 7. The team consists of a qualified PI and team members with adequate technical experience to drive the project deliverables and pathways.
- A solid team of experienced researchers in the field with specifically adjusted tasks is definitely a strength of this project. All milestones and go/no-go points were met, which, in combination with detailed and well-described future plans, substantially increases the team's chances of meeting DOE targets.
- There is a good set of partners with the potential to successfully execute this project. The project is exploring new materials with a hypothesis on how these materials can improve both performance and durability.
- A variety of materials from this project have met the DOE performance target in Milestone 3. The materials being developed and evaluated have set solid progress for continuing work in a relatively short time.
- There is huge potential in engineering a structure that creates well-linked sites with high activity and good support to reduce side reactions or to assist with oxygen intermediate species.
- This project provides an alternative catalyst preparation method that may provide some manufacturing benefits and cost savings. The niobia may improve durability.
- The project contains a focused concept development with good team integration, as well as a clear understanding of the issues.

Project weaknesses:

- To date, there are no measurements on durability. According the project plan, durability measurements are not supposed to have happened yet; however, when a (the) major result of the project is to increase Pt durability by stabilization, it is hard to evaluate the project until durability measurements are made. The project will (and should) have results by next year. There seems to be a lack of "science" in this project, where science might be tremendously valuable to it. The concentration of effort is more of an Edisonian approach to vary the NbO_x weight percent and Pt weight percent (granted, Ford and Edison were friends, but this approach is unlikely to help other projects), at least at this point in time; it seems unlikely that this approach will provide the ability to fully explain results. NbO_x interactions should be understood, and coverage on the carbon should be examined. Understanding the Pt bonding, as well as the degree to which it is on the carbon or NbO_x, seems critical to being able to explain how the system works.
- The limitation of particle size distribution for PVD-made catalysts, both for small- and large-scale batches, is concerning. The team has to focus on controlling the PVD process to achieve narrower particle size distribution. The shelf life of PVD-made catalysts is not known; an understanding of shelf life is important. The catalyst structure of the PVD catalyst in ink and CCMs should be analyzed to understand its structural stability under ink-making conditions.
- The sheer number of variations almost demands a better grip on operational conditions to composition to performance to durability, and could be more suitable for a combinatorial chemistry approach. Good fuel

cell testing also requires an adjustment of ink recipes to obtain the best performance results, extending the matrix further.
- There are questions as to how durable these materials will be and whether catalyst optimization for durability will have a negative impact on the BOL performance presented. It is also unclear how performance can continue to be improved. Much of the future work and many of the upcoming milestones, however, address any weaknesses.
- To date, the project has lacked appropriate characterization to indicate what the structure produced is and to prove or disprove the hypothesis that niobia improves durability.
- Progress is slow, with inconsistent results leading to an unclear development path, as well as the use of conventional carbon supports.

Recommendations for additions/deletions to project scope:

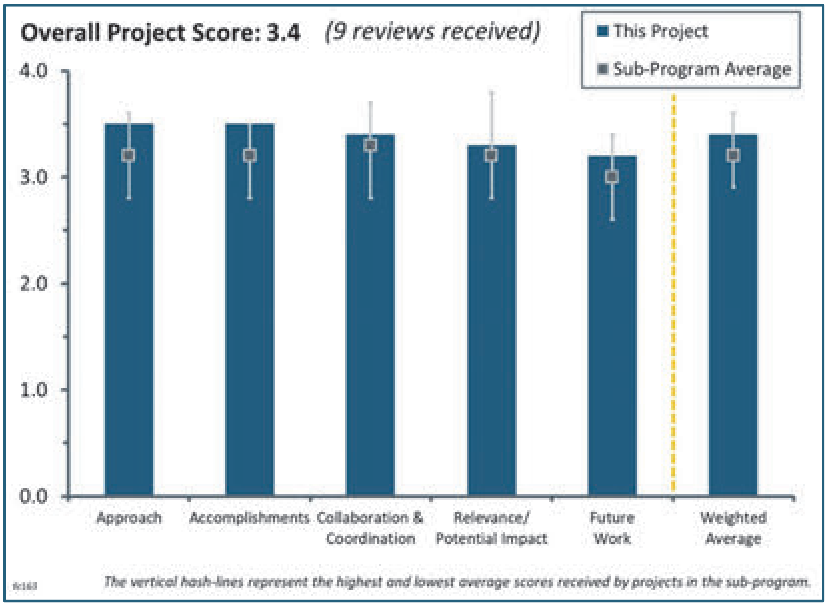
- No changes to the project scope are recommended.
- ORNL has good experience and equipment for thinking a little outside the box on this project scope to anchor sites and gain better control over deposition composition. ORNL team members may thus discover what is really happening in this catalyst system and better understand how this could benefit the goals, and where not. Otherwise, without understanding, the iteration could lead to merely deposition of only more Pt with high surface area, lacking durability.
- More science is necessary; it is important to understand the NbO_x coverage and bonding on carbon and how this affects the carbon porosity. The team needs to understand the Pt bonding and how much is on NbO_x and on carbon, respectively. The Pt bonding interactions should be measured, and durability measurements should be taken (as planned in the future work).
- The following additions will help the project understand the quality of PVD-made catalysts better:
    - Performance stability under load cycling and start/stop cycling
    - Structural stability of the catalyst under the ink-making process
    - Understanding of the shelf life of PVD catalysts
- Work to narrow the particle size distribution could be beneficial.
- The use of state-of-the-art carbon supports is recommended.

Project #FC-163: Fuel Cell Systems Analysis

Brian James; Strategic Analysis, Inc.

Brief Summary of Project:

This project seeks to estimate current and future costs (for years 2020 and 2025) of automotive, bus, and truck fuel cell systems at high manufacturing rates. Analysis projects the impact of technology improvements on system cost, identifies low-cost pathways to achieve U.S. Department of Energy (DOE) automotive fuel cell cost goals, benchmarks fuel cell systems against production vehicle power systems, and identifies fuel cell system cost drivers to help facilitate Fuel Cell Technologies Office programmatic decisions.



Question 1: Approach to performing the work

This project was rated **3.5** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project uses an excellent approach to estimate current and future costs of automotive, bus, and truck fuel cells (for years 2020 and 2025) at high manufacturing rates using the Design for Manufacture and Assembly (DFMA) method. Integrating the latest technical achievements and results of other consortia (DOE-funded projects) and industry contacts gives an overall coherence.
- The DFMA method for cost estimation is very good, and the close interaction with component suppliers and system developers is key to fairly accurate cost estimations. The principal investigator (PI) also keeps broadening the scope based on feedback, which is highly appreciated.
- The team uses a proper combination of fundamental models and component and material test validation to perform analyses. The one issue in the past has been the relative unavailability of state-of-the-art electrodes against which to validate, but that issue has been addressed in the past year or more with access to these materials from the Fuel Cell Consortium for Performance and Durability (FC-PAD) and other DOE-funded electrode/membrane-electrode-assembly (MEA) projects.
- The approach of using system analysis to inform DOE about the current status and opportunities for cost reduction is appropriate for this project. Updating the light-duty vehicle (LDV) model annually, while updating medium-duty vehicle (MDV), heavy-duty vehicle (HDV), and bus system models less frequently, makes sense. The DFMA approach has been refined through the many years this team has been conducting cost analyses for DOE.
- Strategic Analysis, Inc. (SA) has provided a consistent approach of DFMA analysis in its bottom-up cost analysis. Occasionally, SA relies on supplier quotes for comparative evaluations (i.e., perfluorosulfonic acid [PFSA] vs. electrospun polyphenylsulfone [PPSU]), which can favorably bias toward the DFMA analysis. SA actively solicits input from projects and manufacturers to ensure the project makes the right assumptions. SA also consults with the U.S. DRIVE Partnership Fuel Cell Technical Team to ensure realistic system assumptions and technology choices.
- SA does about all that can be done to analyze fuel cell systems. The PI and his team use reasonable methods and models to estimate and project costs and volume cost reduction. The team supplements project research with information from the project's national laboratory partners and the literature.

- The project employs a very structured and regularly updated approach to evaluate the high-volume cost of fuel cell systems. The system topologies and stack performance assumptions are updated to meet the state-of-the-art technology status. Recent trends, such as the use of fuel cells for truck applications, are included in the work.
- The approach to performing the work is on target to solve the technical barriers listed.
- The DFMA method seems like a valid approach to address the cost calculation issue. The project has covered many materials and manufacturing technologies; however, the fundamental assumptions leading to the calculated costs are not stated in the presentation. This absence makes it difficult to assess the relevance of the calculated costs.

Question 2: Accomplishments and progress

This project was rated **3.5** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project showed excellent progress toward identifying the major cost changes year to year. This progress will help DOE achieve its goals by tracking how technology changes increase or decrease cost.
- Validation of the state-of-the-art PtCo-alloy electrode appears strong. Over the past year, the team has performed solid analyses of the high-pressure operation without water vapor transport (WVT) operation, a viable shutdown procedure, and cell voltage cycling mitigation, with a focus on potential impact on system cost. The analysis is sound. There are some questions about the limiting current density assumptions, such as the relative humidity (RH) dependence, but as long as the data is not used far outside the validation regime, there is little concern.
- Most of the work this year involved updating last year’s model, but a few new areas were investigated, with useful results. An alternative membrane support based on electrospun PPSU was investigated and found to be significantly less expensive at high volume than the expanded polytetrafluoroethylene (ePTFE) supports used in the prior year’s analyses. SA also investigated co-electrospinning of ionomers and supports, as well as electrospinning of catalyst layers. These studies were useful in determining that electrospinning is similar in cost to conventional fabrication methods for these processes. An additional side study on physical vapor deposition (PVD) of platinum catalysts demonstrated that PVD synthesis costs are lower than the cost of traditional wet chemical methods.
- SA did a good job updating estimates and projections based on market trends (changing materials and manufacturing costs) and changes in the technology incorporated in fuel cell systems.
- The regular updates of the cost analysis are achieved on track, based on the available information.
- The project showed good progress on LDV and now MDV/HDV cost estimation.
- The project achieved this year’s objectives. Automotive cost adjustment for 2018 and cost estimation for MDV have been achieved, with an expected deliverable for September 2018.
- The defined project goals are met; the overall DOE target of <$40/kW seems achievable for large production volumes for the 2025 auto system.
- SA has made some good progress this year. It was nice to see the team focus on the d-PtCo/HSC (high-surface carbon), which is the most relevant automotive system. There appear to be some discrepancies between the membrane support cost study and the composite membrane costs. It would be good to provide details of all aspects of the process (line speeds, scrap rates, etc.) to understand where the differences lie. It was premature to do a cost study on the PVD catalysts, which have not yet demonstrated decent performance. The medium-duty truck analysis, showing durability requirements leading to higher system costs, was interesting.

Question 3: Collaboration and coordination

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

- SA has done an excellent job of collaborating with the Argonne National Laboratory (ANL) systems analysis project, as well as with several DOE projects involved with component research and development (R&D). The interaction with an extensive list of vendors who have supplied quotes and technical information is also very useful.

- ANL and SA work very well together to conduct coordinated system and cost analyses to determine the optimal system design to achieve the minimum cost. SA consults with many sources to get input for the project model and to get feedback on the technology options the team considers.
- The ANL team works synergistically with the various DOE projects, both to assist those projects and to feed ANL's own model development. The ANL team also builds on the learnings from FC-PAD and feedback with SA in the cost analysis project, as well as with original equipment manufacturers (OEMs).
- The project has good involvement of industry partners for the cost analysis. As the market is transforming rapidly at the moment, special attention should be paid to also include new players (especially on the balance-of-plant component side regarding hydrogen recirculation, air compression, air filtration, etc.).
- The project team has good cooperation with ANL and the National Renewable Energy Laboratory (NREL) on the analysis and results, and the team has excellent contacts with industry.
- The project partners are well engaged and provide valuable input. Industry and national laboratory partners are well represented.
- SA made good use of their partners' input and the literature; however, the scope of the analysis is narrow and is focusing on—virtually locked onto—PFSA polymer electrolyte membranes (PEMs) using hydrogen/air. Maybe this is what DOE wants; however, it would seem prudent to consider competing fuel cell technologies, such as high-temperature PEMs, alkaline PEMs, etc. to see how using these technologies might affect predicted projects and costs, which could guide the approach to market.
- The project has worked with a large spectrum of companies. However, the major state-of-the-art material suppliers are missing (e.g., W.L. Gore, DuPont, Tanaka Kikinzoku Kogyo K.K., SGL Group). Furthermore, there is no comparison between the calculated cost and the reference market prices of component suppliers to validate the calculated numbers.
- The collaboration with ANL is clear, but the role of NREL is unclear. The PI's discussions with other industry developers is critical.

Question 4: Relevance/potential impact

This project was rated **3.3** for its relevance to/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.

- Because cost reduction is, at the moment, the single most important remaining barrier for the market introduction of fuel cell vehicles, this project is extremely important for identifying the major cost drivers and focusing R&D to reduce overall cost. It is also extremely important to provide decision makers, industry, and the general public with verified information on the cost of fuel cell systems at higher production volumes as a basis for strategic decisions and to provide perspective about how the cost can be reduced when moving from very low-volume production all the way to mass-market production. The work is very valuable, and continuing the analyses is strongly encouraged.
- This project provides the Hydrogen and Fuel Cells Program (the Program) with cost and performance annual updates that serve as the key feedback for assessing the state and progress of the technology and, indirectly, the effectiveness of the Program. This project also serves a valuable role as an independent, public validation/verification of the various project efforts. The project also serves to guide other teams in choosing proper operating conditions and regimes for their development.
- Since the Program defined cost and performance targets delineated in the Multi-Year Research, Development, and Demonstration Plan, it is necessary to track the progress toward hitting these targets as the Program progresses. SA is performing this function and doing it in a reasonable way.
- This project provides a powerful tool to forecast the costs for fuel cell systems. The project uses very recent achievements of other projects, which engenders broad consistency. The project aims to identify fuel cell system cost drivers to help DOE to refine and update its targets.
- Identifying the cost drivers that enable fuel cells to meet their expected performance is highly relevant to help target areas that need more research.
- Cost is a key indicator of any technology; this project helps with understanding the progress in terms of costs.
- The relevance of this project is mostly to provide DOE with status updates on the DOE technology portfolio and occasionally to help guide research priorities. More focus on the latter would be

preferable. Direct value to OEMs and developers is limited because they do their own cost studies. Academic and national laboratory projects can use SA to report the cost potential of their concepts when they do not have their own resources.
- The project is useful for estimating cost status and informing DOE, but it does not significantly contribute to technological improvement.
- When costs are transparent, decision makers can orient more easily. The calculated cost is based on the current status of the system analysis. However, the assumptions for the cost calculation are not always clearly stated so that one can comprehend the calculated costs. Material prices are not clearly marked to indicate whether they represent the market price based on quotes or whether they have been calculated. In the latter case, the market situation is not reflected. This might lead to an incorrect assessment when materials or technologies are directly compared regarding their cost effectiveness.

Question 5: Proposed future work

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

- The proposed inclusion of durability into the cost modeling would be a very important step, especially as applications with different durabilities are being discussed (i.e., passenger vehicles vs. buses and trucks).
- The future work is well planned and logical. The proposed addition of durability considerations would be helpful.
- The project has a good handle on where it needs to go. Durability is a great addition.
- The proposed future work listed by the project team is as expected and in line with the results shown.
- The team will continue with support of the annual cost and performance assessments, which is proper. In addition, the team has been tasked with expanding to MDVs, as directed by DOE. While the team is also strongly linked to and supports FC-PAD, more focus on developing the fundamental knowledge that will allow developers and suppliers to continue to improve performance and durability is desirable. Such tasks would include better understanding of the non-Fickian (local oxygen) transport in the electrode, water transport fundamentals, durability fundamentals, and contaminant mechanisms and mitigation.
- Slide 30 says the future work is to “complete studies and final report,” which is good but somewhat vague. Considering the details presented and that there are three more years of work until September 2021, it seems some direction should be offered for the future work. Many things could change in three years. Part of the future work of SA and its national laboratory partners in analyzing fuel cell systems should be focused on examining the trade literature to see whether there are market forces or technical innovations that could radically alter cost estimates and the projections of system performance and costs.
- All the topics in the LDV future work are justified, especially the updated ionomer cost studies and incorporation of durability into cost modeling. It is desirable for SA to prioritize studies to assess the potential cost of systems containing low-technology-readiness-level (low-TRL) technologies (non-platinum-group-metal [non-PGM] anion-exchange membrane fuel cells [AEMFCs]) to help DOE prioritize research funds.
- The proposed future work seems to address additional technologies that have not been calculated so far. A comparison between calculated costs and forecasts of market prices from suppliers for large industrialized quantities throughout the value chain might provide some useful insights about the validity of the cost calculations.
- The proposed future work aligns with the project plan. A cost model for electrospun electrodes is desirable, in addition to the model for electrospun membranes presented this year.

Project strengths:

- The team has excellent experience in DFMA and cost analysis. Excellent interactions with DOE projects and vendors provide extensive information about design of state-of-the-art fuel cell components and systems.
- The project provides an excellent tool for tracking cost and understanding the impacts of changes.
- Extremely valuable cost analysis provides important feedback to identify and prioritize future R&D to drive down fuel cell system cost.

- The team has a very strong grasp of fuel cell fundamentals and model development and application. The project is a strong collaborative effort with FC-PAD. Recently, the team has had good access to some state-of-the-art materials, which will be more relevant for future mechanistic studies, to better populate the project models.
- The project shows a good assessment of fuel cell performance and costs and cost changes with production volume for fuel cell systems based on favored technologies for making a system.
- The project's strength is its good approach to estimating current and future costs of automotive, bus, and truck fuel cells (for the years 2020 and 2025) at high manufacturing rates using the DFMA method. Integrating the latest technical achievements and results of other consortia and industry contacts engenders broad consistency.
- One key strength is the collaboration with ANL to develop a low-cost system. The project provides high value to DOE in assessing system costs as a function of production volume. The approach of the DFMA methodology is another strength.
- The project has strong collaboration with ANL. The cost is being calculated based on the modeling results of an optimal system. The resulting technical assumptions should provide a good and transparent basis for the cost calculation. The project conducts broad analysis of various materials and manufacturing technologies. The project has employed a stable calculation methodology over the years.
- The PI takes feedback from industry and works closely with industry.

Project weaknesses:

- Perhaps one weakness is the lack of access to a full fuel cell system to validate the system-level model, including dynamic operation and durability. Providing access, however, would require a major development effort, which is outside the scope of this project and, perhaps, of the Program overall. The team adequately addresses this weakness with consultations with the OEMs and other system developers.
- The strength is that SA is doing a good, detailed analysis of favored technologies for making a fuel cell system. The weakness is the technical team members are not seeking out possible disruptive forces or technology changes for SA's projections. Maybe seeking out such forces or changes is out of scope, but it would seem wise to search the trade and technical literature more.
- Project weaknesses include the following:
    - The cost degradation seems based solely on higher utilization of one machine, which has a specific capacity. Typically, in the course of technological advancement, smaller machines are replaced by larger ones. Here, it seems that once the capacity of a machine is reached, the exact same machine is then duplicated. Still, one cannot see any step costs in the cost degressions.
    - The commercial assumptions (mark-ups, location factors, value/supply chain) are not stated in the presentation.
    - No reference to a bill of materials or geometrical design of the cells is given.
    - No validation or disagreement of calculated costs by suppliers is discussed, so the relevance of the calculated cost cannot really be assessed.
- One weakness is the comparison of ePTFE using supplier quotes with electrospun PPSU using DFMA. There are apparent inconsistencies within the membrane cost analyses with different supports.
- The model should also integrate system durability and take into account the impact of "degraded modes" on the performance and cost. Lack of validation of the model is a project weakness.
- As it is set up, the project is not likely to lead to technological improvements. It only demonstrates the current status in terms of cost.
- Systems could be refined further with industry interactions.

Recommendations for additions/deletions to project scope:

- As new suppliers for stack and especially system components are entering the market, the project team should try to include more industry partners in the analysis (e.g., inclusion of additional suppliers for system components such as air compressors and hydrogen recirculation). On the stack side, special focus should be paid to bipolar plate coating and sealing processes. Inclusion of durability would be very important, especially for the commercial trucking applications that require long lifetimes. As the technology is progressing rapidly, the project team is encouraged to continue updating system topology and performance data (e.g., MEA power density). Higher power densities are being observed for laboratory stacks and systems, and it is expected that these higher densities will be reflected also in the next state-of-the-art systems that are being introduced to the market. Also, ways to further reduce system complexity, such as removing the humidifier or using only a compressor instead of a compressor/expander module, should be taken into consideration. Attention should be paid that specific performance targets do not drive up overall system cost (e.g., if 9.5 kW/g_{Pt} requires two-stage charging and might affect overall system efficiency as a result of high parasitic power consumption of the compressor, it might be possible to slightly reduce this requirement to benefit the overall system cost).

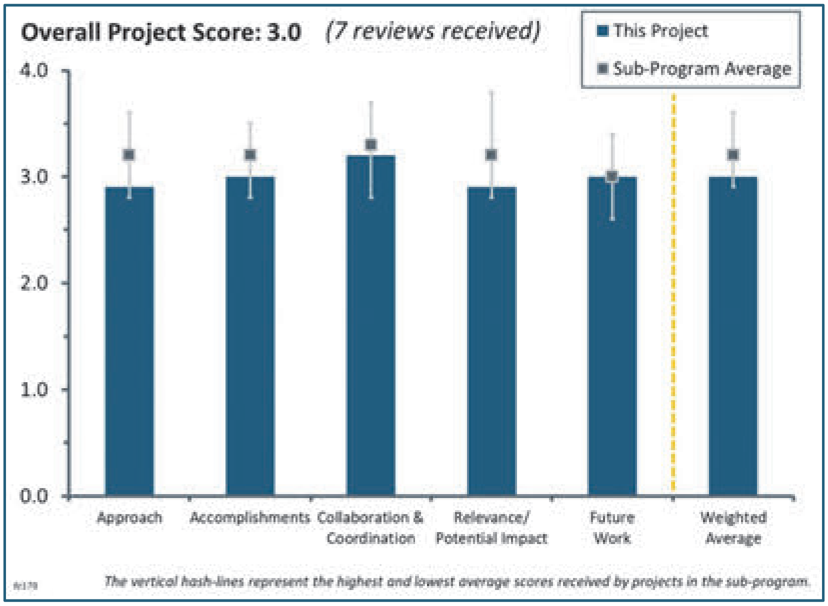
- DOE is investing heavily in low-TRL concepts such as non-PGM catalysts and AEMFCs. SA should run cost analyses (with system support from ANL) to model the cost potential for these systems. These analyses could help define technical targets for these projects. For example, the analyses could show what power density an AEMFC would need to achieve to be cost-competitive with a polymer electrolyte membrane fuel cell (PEMFC) system, considering that the AEMFC system will need a carbon dioxide scrubber and a large humidifier (100% RH in required). Such analysis could also show what power density makes a non-PGM PEMFC cost-competitive with a Pt-based system. SA is uniquely qualified to conduct such analysis, without which it is difficult to justify DOE’s investment in these technologies. SA should provide a clear, detailed table for the costs of all the components in the same units (dollars per system or dollars per kilowatt). The team should use Pareto analysis to determine which components warrant R&D for likely cost reduction. The team should revisit seals and gasket costs because SA’s current projections are too low.
- Greater focus is recommended on contributing to the fundamental knowledge base, including mechanistic understanding of performance and durability limiters and enablers such as local oxygen transport, water transport, and electrode and membrane degradation and contamination. It would be interesting to see a cathode stoic sensitivity study on cost and performance to address the wide range of stoics shown in various presentations (ranging from about the 1.5 of this project to as high as 2.5) and to focus teams on a more relevant and productive value.
- The team should search trade and technical literature more for alternative or disruptive technology and estimate the cost and performance changes relative to favored technology as a benchmark.
- The model should integrate system durability and take into account the impact of degradations on the performance and cost.
- For the presentation of the cost degression on slide 7 or the waterfall chart on slide 8, a cost breakdown into material cost, manufacturing cost, and mark-up cost would be very helpful.

Project #FC-170: ElectroCat: Durable Manganese-Based Platinum-Group-Metal-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells

Hui Xu; Giner, Inc.

Brief Summary of Project:

The project objective is to develop a Mn-based platinum-group-metal (PGM)-free catalyst and membrane electrode assembly (MEA) as a replacement for current PGM catalysts. The developed catalyst and MEA will have lower cost/cost volatility, improved corrosion performance, improved demetallation performance, and reduced membrane degradation compared to the baseline. The developed catalyst and MEA will be tested on a development fuel cell stack.



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 **2.9** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project approach is appropriate, consisting of material synthesis, characterization, and modeling. Inclusion of durability as a key parameter for design of catalysts adds significant value to the approach.
- The development of effective Mn-based catalysts could reduce MEA costs compared to the current dominant PGM-based catalysts. Hence, the objectives to enhance the performance of Mn-based catalysts via systematic and integrated investigation is very appealing. The team has a well-defined, but possibly too optimistic, pathway toward identifying and producing the desired catalyst materials.
- All project objectives have been clearly identified, and the approach is carefully designed to address all of them.
- The development of Fe-free catalysts has been a key need. The inclusion of computational work is good, but the work seems lacking in rigor and relevance. The synthesis work is very promising, even while details are lacking. Comparison to Fe-based systems is needed. In addition, the inclusion of and reliance on MEA results is good.
- Giner, Inc., will address the U.S. Department of Energy mission on development of PGM-free oxygen reduction reaction (ORR) catalysts, which should have intrinsic activity similar to state-of-the-art Pt/C (at low loadings). The technical targets the project will achieve by the end of funding period are performance-based (>0.044 A/cm^2 at 0.9 V).
    - Despite the project’s being specifically dedicated to catalyst durability, the final measurable durability targets were not clear. It is unclear whether the plan is to improve durability by 50% at all Multi-Year Research, Development, and Demonstration Plan design points (potential cycling and carbon corrosion).
    - The demonstration of rotating disk electrode (RDE) data with ORR performance of Pt/C, FeNC, and MnNC (probably in acidic electrolyte) is a weak argument for Mn catalysts’ potential 50% higher stability. The carbon produced during pyrolysis in the case of Mn will be less graphitic (Mn does not promote graphitization), and carbon corrosion will be more pronounced for Mn-N-C catalysts.
    - The technical approach is based on initial density functional theory (DFT) calculations, which will be used for the synthesis of MnNC catalysts, followed by scaling up, MEA fabrication, testing,

and finally validation by the original equipment manufacturer team member. Despite the fact that Task 1 (ab initio calculations) will be performed for all 36 months, Tasks 2, 3 and 4 are weakly connected to the expected results of these DFT modeling studies.

- While finding alternatives to Fe-based PGM-free catalysts is not without merit, first demonstrating that current Fe-based PGM-free catalysts actually do cause increased membrane degradation seems prudent. This does not mean simply stating that Fe is a Fenton's catalyst but rather providing direct experimental evidence that state-of-the-art Fe-based catalysts result in MEA degradation. In addition, based on the technological maturity of this catalyst, the "cost analysis" to be performed by General Motors (GM) seems a little premature. However, if the cost model is supplied at the end of the project, this could be of use to more mature PGM-free catalysts. (It seems likely the model will show that no PGM-free catalyst is yet cost-effective at the stack/system level because of low performance/durability.)
- The project is focused on development of a durable non-PGM catalyst that exceeds the durability of Fe-based non-PGM catalysts. Although the project objectives and critical barriers are clearly identified, they are not clearly addressed. The project design is based on theory predictions that Mn-based catalysts are more durable vs. Fe-based catalysts. However, this theoretical prediction was not clearly communicated. Another flaw in the project design is that the catalyst with lower activity (MnN_4 vs. FeN_4) is selected for investigation.

Question 2: Accomplishments and progress

This project was rated **3.0** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The team has made good progress in development of new Mn-based catalysts with improved activity and, more importantly, improved durability in RDE testing. Additional durability testing in MEAs is critical and appears to be part of the second year of work. The modeling has appeared to result in identification of potentially preferred active sites, and characterization (both electrochemical and physical) appears to be providing good insight.
- Progress across the project has been very good, with identification and initial testing of two possible Mn-based configurations.
- Significant progress has been made during the last year. The principal investigator (PI) has coordinated all efforts with the collaborators well and has managed to execute a number of structural and electrochemical tests for Mn-based PGM-free catalysts. The projected milestone in this year was met, and the go/no-go decision point of 10 mA/cm^2 was exceeded. The project seems to be redundant in light of ongoing Electrocatalysis Consortium (ElectroCat) activities and combinatorial screening of PGM-free systems. For that reason, the approach to focus exclusively on Mn-based PGM-free system is not well justified.
- The computational work is lacking. Recreating previous work and not doing so better, or with more rigor, begs the question of what the stabilities of the different sites are.
  - The following are also unclear: why C14 is "promising"; how these materials and structure compare to Fe, which has been proven best so far; and whether multilayer structures were checked for all, or C10 was calculated in multilayers to allow CN_5C_{10} to form.
  - The synthesis work is interesting, with many materials made, but the connection between the raw materials, processing, and results is very unclear from the data presented.
  - In addition, some very high peroxide levels are seen (example on slide 10), and since Mn is a peroxide scavenger, it is unclear whether this is a mixed H_2/H_2O_2 fuel cell. If so, it seems that the peroxide would corrode the carbon catalyst locally.
  - There is another big question about the purity of the Mn, i.e., whether any Fe is present. Inductively coupled plasma of the precursor salts and analysis of the catalysts for Fe is needed. The inclusion of 0.7 V and 0.8 V holds on slide 12 is great, but it is unclear why the degradation paths are different. This suggests that the currents are so low that the percent plotted is deceiving as to catalyst instability. This low stability is suggestive of unstable active sites or possible peroxide-caused corrosion, which needs to be addressed.
  - While having MEA work is great, the results so far are quite strange, with rapid drop-off at high potential that is suggestive of either a need for ionomer–carbon ratio and electrode structure improvement, or catalyst instability masked by polarization. Hold tests at different partial

    pressures, at 0.65 V, are needed. In general, the team should be more careful in drawing conclusions. This is nice work.

- Significant progress has been made toward using modeling to identify Mn-containing active sites. A significant improvement in synthesis was achieved that allowed the introduction of more active sites, as indicated by results of RDE tests.
    - There were not many accomplishments in terms of durability demonstrated during of constant potential hold experiments, as potential cycling was required every 20 hours to refresh the surface.
    - There is no clear evidence that the Mn-based catalyst performs better than Fe-based in terms of hydrogen peroxide generation, because RRDE experiments were performed on thick films with a loading of 0.8 mg/cm^2. There were not many accomplishments in terms of fuel cell performance demonstrated, and no clear path for its improvement was proposed.
- The performed work according to the statement of project objectives was reported. The role of DFT calculations in achievement of the project and DOE goals is unclear. The interpretation of results (summarized in Milestones 1.1 and 1.2 [M.1.1 and M.1.2]) is incorrect and generic. The structures in M.1.2 were not predicted; these structures have a convergence minimum according to input parameters in the WASP code, while geometries were proposed and used as initial coordinates input. The achievement of the M.1.1 goal on “key descriptors” is irrelevant to project targets and does not have scientific value. These descriptors are used for calculation of reaction pathways for more than 30 years, and Professor Norskov has comprehensively used them for ORR DFT calculations since 1993. Despite the DFT-predicted very specific configurations of Mn-N active centers with exact numbers of N- and C- atoms, the synthetic approach selected is generic, with no ability to precisely control formation of required structural fragments. The statement that introduction of extra Mn ions will increase performance is incorrect unless there is experimental evidence that all Mn atoms will be utilized in the Mn-N active centers. The series of experiments with extra Mn addition and correlation with improved performance should be carefully re-evaluated. The team did not take into account that zeolitic imidazolate framework (ZIF)-8 and all Mn precursors have substantial amounts of Fe. According to the certificate of analysis on ZIF-8, it may have up to 0.1 wt.% of Fe. Manganese nitrates and acetates can have up to 2 wt.% of Fe. The dramatic increase of Mn precursors up to 20 wt.% in combination with ZIF-8 results in the formation of Fe-N centers, which provide the ORR activity. Several studies on this subject are available. The rotating ring disk electrode (RRDE) clearly indicates the presence of H_2O_2, despite the highest loading of catalyst ever reported (0.8 mg/cm^2, while the community standard is 0.6 mg/cm^2), which means MnNC catalysts are not selective in the 4e$^-$ reaction and intrinsically have low mass activity.
- Performance/activity remains a large concern. Additionally, while it is stated that the catalyst shows enhanced stability versus Fe-NC, the end-of-test performance looks essentially the same. Thus, a large focus on improving catalyst activity is still required. However, it is not clear how the team will achieve the necessary activity improvements. The main approach appears to be increasing Mn doping. However, drawing from knowledge of the Fe-based PGM-free catalysts, it appears this approach is somewhat risky (maintaining decent Mn dispersion will be challenging). If this (somewhat) risky approach fails, it is unclear what the backup plan is.

Question 3: Collaboration and coordination

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

- The presented results indicated very good cooperation among the partners and significant supporting work performed by five national laboratories through ElectroCat.
- Team members have planned and scheduled meetings well, and the PI manages the project effectively. The established collaboration with ElectroCat facilitates the understanding of ORR activity in this class of catalysts.
- Good collaboration is evident, but more feedback between DFT and synthesis, catalyst structure, and MEA will be better.
- Collaboration between the participants is very well coordinated.
- This is a well-coordinated effort between industry and academia.
- Overall, collaboration appears appropriate. One question is whether the modeling results are being used to guide the material synthesis toward designing catalysts with preferred active sites.

- The partners are well engaged and are working with ElectroCat members. GM currently does not appear to be highly engaged in the project, but that is understandable at this stage of the work. Hopefully GM's electrode design work can help to overcome the very low MEA performance.

Question 4: Relevance/potential impact

This project was rated **2.9** for its relevance to/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.

- The proposed technology may have an impact on the DOE Hydrogen and Fuel Cells Program (the Program) mission if it will be carefully re-evaluated.
- The project does provide an alternative to the more conventional Fe-based PGM-free catalysts. However, there does not appear to be sufficient evidence that activity/performance can be improved to the required levels, and even if that occurs, there still does not appear to be any evidence that replacing Fe is necessary (it may be, but currently, it is just an assumption).
- Overall, the project is relevant to addressing the primary cost, durability, and performance barriers for fuel cells. It is unclear whether non-PGM catalysts will ever be durable enough for commercial viability. Demetallization and carbon corrosion may be intractable issues. These concerns are not reflective of the work done in this project specifically, but the field needs to reconcile this for the non-PGM approach to have significant potential impact over the next decade.
- Providing the current studies can demonstrate sufficient durability of one or more of the Mn-catalyst configurations, this project would prove very useful to providing lower-cost MEAs and potentially fuel cell systems. However, several aspects on stabilities during operation seem more or less problematic. Hence, there remains an issue as to whether these catalysts can deliver as promised.
- To be focused just on the system with Mn does not look like a compelling case for the project, even though the work itself has been executed in excellent manner. For that reason, it would be difficult to predict that this project, which is focused on the Mn-based carbon catalyst, would make a significant impact on the Program.
- The move away from Fe to Mn in the project is very important, but greater care should be taken to achieve relevant performance tests.
- Although the project is relevant to DOE goals on durability and cost reduction of a fuel cell catalyst, multiple problems with performance and durability at the initial stage of the project make the potential impact of this project unlikely to be high.

Question 5: Proposed future work

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

- The proposed future work is well aligned with meeting project objectives. Giner, Inc., should consider increased focus on MEA-level durability assessments, including potential cycling and support stability, to demonstrate improved durability in relevant environments rather than RDE.
- The tasks outlined in the future work plan appear reasonable and should allow for the necessary demonstration that Mn-based catalysts could be viable non-PGM catalysts on MEA devices.
- Future work is in line with ongoing activities, and it is well planned.
- The DFT part of the project is questionable. The results of calculations cannot be used as a feedback on catalyst preparation because of the fundamental lack of control of the atomic structure in high-temperature synthesis. The proposed action items on catalyst synthesis and MEA design are relevant to the project goals.
- The future work is not explicit enough to evaluate, especially in the modeling section. Key recommendations are more rigorous structure stability versus reaction pathway comparison, testing for Fe contamination, more rigorous RDE and MEA tests, and diagnostic tests such as stability at different fluxes at the same potential to determine active site stability and turnover frequency.
- Project plans contribute to overcoming some barriers but lack specificity.

- The performance at the MEA level is concerning. The performance is due to either very poor catalyst activity or poor electrode design. The team members should attempt to make an MEA using a state-of-the-art Fe-based PGM-free catalyst to help clarify how much of the gap is from the project catalyst versus catalyst layer design. If the catalyst is the problem, all efforts should be focused on improving activity, as it is currently far too low.

Project strengths:

- Synthesis, characterization, and electrochemical evaluations in RDE and MEA are very well executed. The modeling part is a world-class science, and the PI who did that part should be praised for this work.
- The project team has an appropriate balance of modeling, synthesis, and characterization. The approach has led to identification of a catalyst with potentially higher durability than the incumbent, based on RDE testing.
- There is a strong modeling component in the project. This is a very strong team of experts in modeling, synthesis, catalyst, and fuel cell testing.
- This appears to be a well-balanced and -integrated study focused on improving the performance and durability of Mn-based catalysts for MEAs. The capabilities of partners and collaborators seem to be fully utilized.
- This project provides an alternative to conventional Fe-based catalysts. There are strong team members with different skill sets.
- The shift to Mn-based catalysts is great, and good progress was demonstrated.
- In general, Mn active centers can be used as heterogeneous hydrogen peroxide scavengers.

Project weaknesses:

- The main weakness of the project is significant disintegration between the proposed tasks, milestones, and go/no-go decision points. Tasks are not logically connected, and results of milestones do not effect progress toward project goals. As an example, up to now the project did not benefit from DFT calculations.
    - Another broken link is in the task on catalyst optimization with increase of Mn content. It was reported that RDE evaluation confirmed better performance, per the volcano plot (20% is better than 30% and 10%). However, future work proposes again to increase Mn content. Perhaps this means that 20% is not better than 30%, as presented in the 2018 Annual Merit Review (AMR) report.
    - The unawareness of recent literature on PGM-free ORR catalyst development (which has new trends compared to 2015–2017 hypotheses) is unacceptable for participants in such an important DOE mission project. Recent publications from Norskov, Shuhui Sun, Zelenay, and Banham have exceptionally good information that will help the PI and team to rebuild the project.
- The project design is based on DFT modeling, which does not take into account the real fuel cell environment, such as the presence of water molecules on the surface and potential. So far, DFT modeling has succeeded mostly in interpreting experimental results rather than in predicting new catalysts.
- Evidence for the need to use Mn-based PGM-free catalysts is somewhat lacking. While Fe is a Fenton's catalyst, it is still unclear whether Fe in current Fe-based PGM-free catalysts really causes increased degradation. The MEA performance of the Mn-based catalyst is concerningly low. Significant improvements are required in the coming months.
- Additional focus should be placed on assessing durability (potential cycling, carbon corrosion) in the MEA to determine the feasibility of the approach for commercial applications.
- The computational portion contribution, rigor, and ability to predict are unclear. Since stability and intrinsic performance for Mn systems is unknown, there should be a better effort on this side of things.
- This project has ambitious goals and a substantial breadth of materials options to investigate in a rather limited period of time. The probability of undesirable reactions of the Mn species still seems quite high.

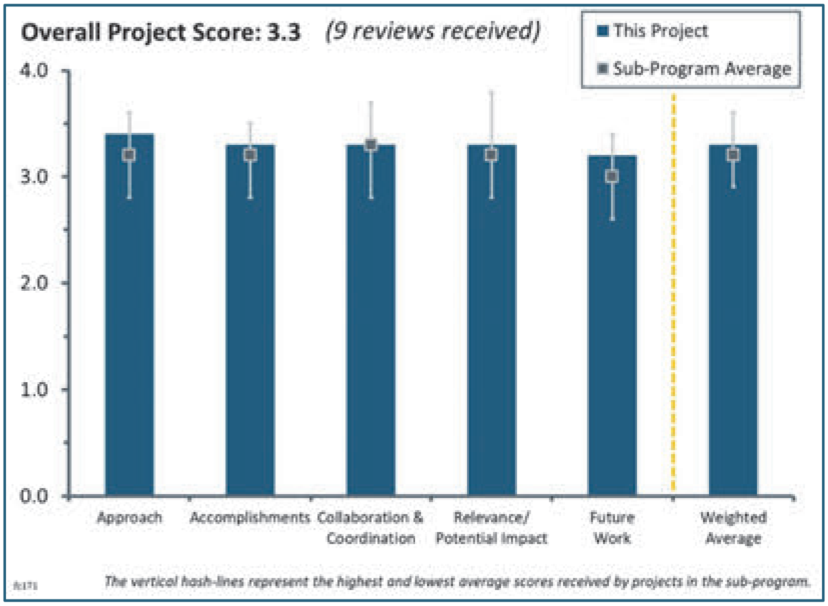
Recommendations for additions/deletions to project scope:

- The team should be allowed to continue pursuing the directions and tasks as described during this AMR report. However, it is recommended that a detailed review of status be performed with all members and key collaborators by December 2018. This would allow for a thorough evaluation of how the materials and test devices actually behave. Then the team can down-select to the one or two very best candidates during the remainder of the second year of this project.
- Additional focus should be placed on assessing durability (potential cycling, carbon corrosion) in the MEA to determine the feasibility of the approach for commercial applications.
- If possible, the reasons for fast catalyst degradation at constant potential RDE tests need to be identified and addressed.
- Better baseline testing would be helpful (perhaps Los Alamos National Laboratory can share its Fe-based PGM-free catalyst).
- A shift to methods that do not rely on a metal–organic framework should be considered.
- It is recommended that the project expand the scope toward more diverse PGM systems.

Project #FC-171: ElectroCat: Advanced Platinum-Group-Metal-Free Cathode Engineering for High Power Density and Durability

Shawn Litster; Carnegie Mellon University

Brief Summary of Project:



This project is developing platinum-group-metal (PGM)-free oxygen reduction reaction (ORR) catalysts for polymer electrolyte membrane (PEM) fuel cell cathodes. A thorough approach that combines advanced, atomically dispersed metal–organic-framework (MOF)-derived Fe-N-C catalysts, PGM-free specific cathode architectures, and advanced ionomers is being undertaken. This project seeks to (1) enable high-power density and improve durability with new cathode structures designed specifically for PGM-free catalysts; (2) increase PGM-free catalyst activity and stability through novel synthesis approaches, including using a simplified, low-cost method; (3) mitigate PGM-free cathode flooding for fast oxygen transport across thick electrodes; and (4) integrate advanced ionomers into the electrode structure for optimal performance and durability.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project appears well constructed, and the strengths of each team member appear to be well utilized. The modeling and experimental work are highly complementary to each other and clearly well-thought-out. Relevant accelerated stress tests (ASTs) are being used.
- The approach of the project is based on re-design of the cathodic catalyst layer (PGM-free oxygen reduction reaction materials) to improve overall fuel cell performance. The approach itself and objectives are clearly described. The main barrier to obtaining higher performance was identified as mass transfer losses, and a mitigation scenario was proposed.
- The presentation was well organized and comprehensively described the various technical efforts under way to address the project milestones shown at the start of the presentation. The various scientific advances and efforts appear to be contributing to the overall membrane electrode assembly (MEA)-based project milestones. Use of MEA modeling is a nice guide for the various efforts, in terms of assessing their impacts.
- The project applies the approaches developed by the investigators from previously funded DOE projects. The approach is sound and helpful in improving understanding of catalyst and MEA development in this field.
- The approach to improving high current density (HCD) is rational. Use of tomography, other characterization, and validation with MOF building blocks seems promising.
- The approach is outstanding, combining synthesis, characterization, and modeling.
- A state-of-the-art (SOA) PGM-free catalyst was received and used to demonstrate performance. The catalyst is then developed and the batch size scaled up to larger batches for catalyst layer and MEA development. This is a very complicated process that could have benefitted from strong technology transfer from the original developer.

- The team's approach of leveraging modeling insights to improve MEA performance is a strong point of this project. A weakness is that the approach is focused mostly on the highest-activity PGM-free materials but these materials seem to be inherently unstable under typical operating conditions. Based on initial results, it seems likely that the project will result in a high-performance PGM-free MEA, but the durability will be as poor as that of previous high-performing PGM-free MEAs.
- The approach seems to be proper to solve the mass transfer overpotential issue with the PGM-free cathode catalyst layer. Water management is a significant issue.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project has an excellent start with the accomplishment of milestones so far. Excellent catalysts are available with interesting properties (Fe-free, single-step process) compared to others in the field, and there are new synthesis approaches. Challenges of transport are clearly identified.
- It has been less than a year since the project started, but the project has made good progress and is mostly on track. It is good to see some durability work. More work in this area is encouraged.
- The project has a good start, thanks to the early involvement of a number of investigators from previously funded DOE projects. The results are promising.
- The goals of the project align well with those of the Electrocatalysis Consortium (ElectroCat). The project is on track, considering the first go/no-go is not until September and the team is within reach of those targets.
- The strong focus on catalyst layer design improvements is highly encouraging. In particular, the focus on new methods to deal with water removal in these relatively thick PGM-free catalyst layers will be of use to all PGM-free researchers. While there are concerns about Fe, the concerns amount to one of the least pressing issues at this time. Also, the ionomer work will be critical, but the initial results are rather confusing. It is unclear why the electrode conductivity shows no dependence on ionomer equivalent weight.
- Technical milestones were clearly presented, and progress against those milestones was described well. A challenge is that the stretch goal for the end of the project (450 mW/cm^2) is still >2x below the PGM baseline, so even if the stretch goal is reached, it is not clear whether additional work would then be justified.
- This project has met the initial half-wave-potential goal of 0.87 V vs. the reversible hydrogen electrode, but the power produced is well behind that shown by other developers. The project appears to be falling behind schedule, which puts further targets and the go/no-go decision in jeopardy.
- The project is mainly on track, according to the schedule. However, current density at 0.9 V is still far away from the milestone and first go/no-go review target.
- The project identified sensitivity for hydrophobicity.

Question 3: Collaboration and coordination

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

- Key personnel are qualified, as demonstrated by their publications on work in this and related fields, but they need to reach out to teams that are further along in the development of this type of catalyst, such as ElectroCat and the Energy Materials Network (EMN) consortium members (national laboratories). The proposal clearly and completely defines the roles and contributions of each team member; the final team, facilities, and equipment required to complete this project are fully in place, ready, and available. This project has full commitment from the partners' senior management and corporate officers.
- The project is well managed, and multiple collaborations, including ones with ElectroCat and EMN consortia, were established.
- The project partners all bring different expertise and have all been integrated well into the overall project. The project should engage more with the National Renewable Energy Laboratory and Los Alamos National Laboratory to understand the ionomer results a little better.

- The collaboration with the University at Buffalo is excellent, and there is some collaboration with 3M. It is not clear how Giner, Inc. (Giner) fits in just yet—whether scale-up is planned or accomplished.
- The team is strong and includes investigators with good electrocatalysis and engineering backgrounds.
- It appears the project is well managed, and the various efforts are well integrated.
- Collaboration is good. The role of each partner is clear.
- The team has complementary capabilities, and the members appear to work well together. One concern is that, other than Dr. Litster's work and switching Mn for Fe, it is not clear how different this project is from the Giner-led ElectroCat project. The work may be overlapping. It is okay if the project leverages that work, but the team should make it clearer that the two projects are not being funded to do the same work.

Question 4: Relevance/potential impact

This project was rated **3.3** for its relevance to/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.

- Increasing overall PGM-free catalyst performance by a factor of four will have a dramatic impact on the entire Hydrogen and Fuel Cells Program (the Program). The new generation of electrodes will be considered a genuine and inexpensive substitute for platinum at the cathode.
- A PGM-free catalyst is critically important for commercializing fuel cells. Fe-doped MOFs have shown significant progress, and additional performance and stability improvements are required. Focusing on water management and other mass transport issues will provide significant benefits for this technology.
- The project strikes an excellent balance between catalyst development, catalyst layer modeling, and catalyst layer design. Thus, while challenging targets have been set, this project is well positioned to close remaining gaps in performance and durability.
- A PGM-free catalyst with improved activity and durability will lead to fundamental changes in the fuel cell industry.
- This project addresses long-standing issues in transport limitations of proton motive force electrodes, including problems with hydrophilicity and ionomer utilization.
- The project is clearly aligned with the "PGM-free cathode" goal for the Fuel Cell Technologies Office, but a concern is whether reaching the stretch performance goal would truly challenge the SOA, because the target performance is still well below the PGM value. Perhaps the technology could be more relevant for stationary applications in which power density is less of an issue. However, a lower power density will drive up cost in components (membranes, plates, etc.).
- It is too early in the PGM-free catalyst area to see a perspective for automotive application. The effort to improve mass transport loss is relevant to general objectives.
- The goals of the project are relevant to DOE goals for ElectroCat. The potential impact is a concern, as it is not clear whether the approach is novel enough to substantially improve durability issues.
- As the iron-based M-N-C catalyst is unstable and has insufficient volumetric activity, it is unclear whether the learning and development on HCD from this project will ultimately be of any value.

Question 5: Proposed future work

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

- The proposed future work all appears reasonable and well justified by the milestones.
- Future activity is well planned and justified.
- The proposed direction is suitable for research in this area.
- The team needs to address durability, which is the plan for next year. It would be good to see progress toward this in next year's presentation.
- One of the largest (catalyst-level) challenges for PGM-free catalysts is to increase site density. Thus, a strong focus should be placed on demonstrating that active site density can be increased without compromising turnover frequency.
- Introducing higher-stability carbons is a good idea, but the project could experiment with carbonization of the existing catalyst (if that has not already been done). Reporting measured active site density and how

that varies with synthesis parameters would help with understanding activity enhancements. The mesomorphology of the catalyst particles should be understood through adsorption and intrusion studies. The mesoporosity is likely quite low. The project should explain why a particle size of 100 nm is optimum. Dramatically reduced particle size, perhaps below 50 µm, should improve ionomer coverage and utilization.
- In future work, the investigators need to reach out to teams that are further along in the development of this type of catalyst, such as ElectroCat and EMN consortium members (national laboratories).
- A more specific idea to improve water management is necessary.
- The project has just started, and there is much left to be done.

Project strengths:

- The presentation was well organized and clear. The team appears well organized. Technical milestones are clear, and progress appears to be honestly assessed against those milestones. There are nice technical highlights.
- The project will develop a predictive method on integration of PGM-free catalysts into the MEAs. Suppressing the flooding will achieve a significant increase in activity of these MEAs.
- The project has a strong team with complementary capabilities. The principal investigator's modeling knowledge can be applied to develop higher-performing MEAs with these PGM-free catalysts.
- The project team is strong in synthesis, scale-up, characterization, and modeling. The project has good integration with ElectroCat and excellent plans for future improvements.
- The project has strong partners and a good balance of catalyst synthesis, catalyst layer modeling, and catalyst layer design.
- This project group is very experienced in scale-up of laboratory processes and in MEA development and fabrication.
- A strength of this project is the ability to analyze the structure of the cathode catalyst layer, including its hydrophobicity nature.
- The project has a very good start.

Project weaknesses:

- There are minor weaknesses: (1) further characterization of the catalyst layers would be helpful (performance at various relative humidities); and (2) while the modeling work was well explained, further insight into the experimental results would be helpful, e.g., the impact of the ionomer, the proposed mechanism of degradation (the team observed no change in cyclic voltammetry before or after the AST, and flooding was ruled out, so it is unclear why the MEA is losing performance), etc. A stronger focus/path toward increasing active site density is required.
- The only high-level concern is whether, if the stretch goal is reached, that is enough to change the thinking about what is possible with PGM-free cathodes and to justify future work and funding, given the lower power density, thicker electrodes, etc.
- A mesoscale focus is needed, through characterization of catalyst morphology at that level. This team is very capable of addressing this issue.
- There appear to be a number of investigators involved in more than one project in the same research area of the Program. A clear separation of focus and resources is needed.
- It is possible that the materials on which the team is focused will have poor durability. It is not convincing that the Fe-N-C materials will be made stable simply by modifying the carbon.
- This project needs to develop and strengthen the technology base for the Fe-doped MOF-based catalyst.

Recommendations for additions/deletions to project scope:

- The scope is appropriate.
- As durability and deactivation mechanisms become more apparent through ongoing ElectroCat projects, the team may need to modify the catalyst compositions being examined, including focusing on non-Fe catalysts or other modifications.

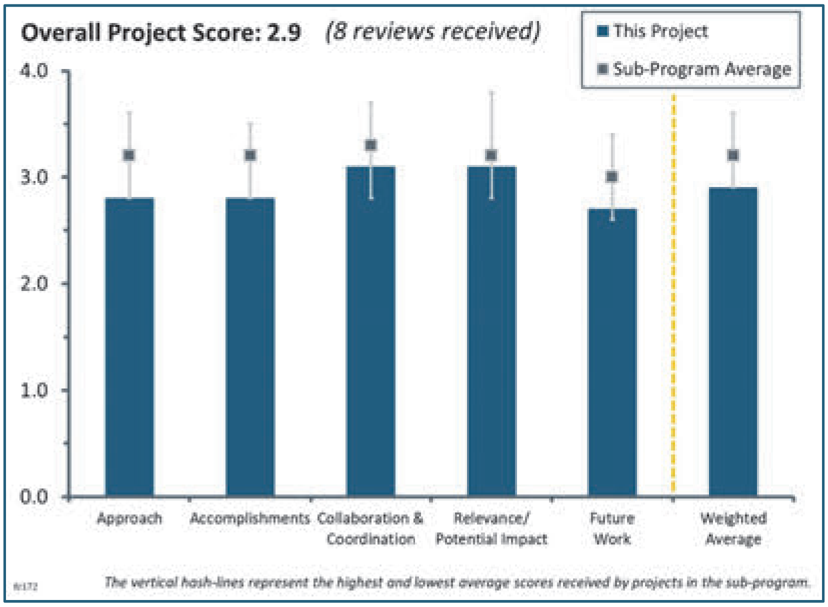
- The recommendation is to focus more on knowledge development in terms of structural implications for mass transport overpotential rather than developmental efforts to achieve the target. This is long-term research; an instant accomplishment would not be expected.

Project #FC-172: ElectroCat: Highly Active and Durable Platinum-Group-Metal-Free Oxygen Reduction Reaction Electrocatalysts through the Synergy of Active Sites

Yuyan Shao; Pacific Northwest National Laboratory

Brief Summary of Project:

The project objective is to improve the activity and durability of platinum-group-metal-free (PGM-free) oxygen reduction reaction (ORR) catalysts through dual-active sites for enhanced oxygen reduction and hydrogen peroxide (H_20_2) decomposition. Materials and synthesis innovations include (1) dual active sites for ORR and H_20_2 and (2) thermal shock activation for high activity through increased active site density. The developed catalysts will lower cost, reduce H_20_2 formation by 50%, maintain the activity level, and double the durability compared to baseline platinum catalysts.



Question 1: Approach to performing the work

This project was rated **2.8** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project team is focused on identifying pathways to produce catalysts using a thermal shock activation technique. This project's focus is to cut H_2O_2 formation by half (versus Pt catalysts), while maintaining the same activity and doubling the durability compared to the baseline. The scale-up of the shock activation technique was not demonstrated.
- Thermal shock activation "freezing" N in a non-equilibrium state is an interesting idea that has been previously explored by others, although not with a duration as short as this project.
- The approach is based on a two-stage ORR assumption, and it is well understood. Thermal shock activation should be described and hypothesized clearly.
- The goals of the project align well with the ElectroCat Consortium (ElectroCat) mission. It is realistic to think that peroxide formation is a source of deactivation in these materials. The approach the team is pursuing is a logical way to address the peroxide formation. While the approach is logical, it is a concern that the initial results do not clearly show that the peroxide decomposer solves long-term degradation in a membrane electrode assembly (MEA). Even if the initial MEA performance was poor, the team should show a clear side-by-side comparison of MEA degradation for the project approach, versus the standard catalyst without peroxide decomposer, to see if the decomposer makes a significant impact in the real-world environment. The project team showed rotating disk electrode results, but a simple MEA test would have been much more convincing.
- Objectives and barriers, in terms of the catalyst design and performance, are well defined. The importance of "Thermal shock activation for high activity by increasing active site density" needs to be more clearly described; it is unclear why this approach is important and what its effect will be.
- The incorporation of two different types of active sites with different functionalities, thereby pushing activity and durability, is promising, but it is not a new idea. If successful, it could dramatically improve the durability of non-PGM ORR catalysts. However, based on the presentation, it is unclear how the current proposed work will be successful. The current limitation is the efficient dispersal and integration of two

different types of active sites into a single catalyst. At this point, the project team has simply mixed particles of the two different types of catalysts and observed modest success. In the future work, the team proposes a molecular-level integration of the dual active sites; however, no feasible methodology for accomplishing this is presented. All proposed future work is a bit vague. To this point, the group has used the standard pyrolyzed metal–organic framework (MOF) catalysts presented and developed by other groups. However, the project's activity is far below that of other groups. Before going any further, the team should rectify this difference to attain reasonable ORR activities. Electrically induced thermal shock is proposed to aid the retention of a higher nitrogen content. While it is a nice idea, it does not seem to be practically feasible. Not only is there no clear link to the rate of thermal treatment and nitrogen retention, but it is likely that the proper removal of Zn, which is required for material porosity and to attain high activity, is not possible with this technique. The project team should move on to a different synthesis process and drop thermal shock from the project.

- The approach advantages, differentiation, and risk mitigation are not clear. It appears that the main differentiators are the incorporation of peroxide scavengers/decomposers to deal with low selectivity of PGM-free catalysts and rapid heating/cooling to "thermally" lock active sites. There are fundamental problems with both approaches:
    - It is not demonstrated that peroxide decomposition will protect the active sites, ionomer, and membrane sufficiently.
    - There is very little proof, if any, that thermal shock is a viable approach. Rather, the fundamental approach of trying for rapid heating, a kinetic bypass of more a thermodynamically active site formation, in the hopes of achieving a thermodynamically unstable and possibly more active site, is problematic, since this is not a durable catalyst. The latter is a really flawed approach.
- The approach is poorly described, raising multiple questions about the selection process for these tasks.

Question 2: Accomplishments and progress

This project was rated **2.8** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Catalysts with Fe and Co were identified as most active (this is well known from literature), and two H_2O_2 scavengers were selected. Taking into account that CeO_x is widely used by original equipment manufacturers on the cathode side, tantalum-doped oxide can potentially be of interest for improving electrode durability.
- Two effective hydrogen peroxide composers were identified.
- The project has a good start.
- The project is hitting the milestones, as defined, with the exception of the thermal shock approach (which may not be relevant to the project anyway). The absolute E1/2 should be used in future milestones, as using E1/2 versus Pt/C leads to ambiguity. The Pt/C E1/2 can be different for various catalysts and is known to be lower in sulfuric acid than in perchloric acid.
- The project team has demonstrated satisfactory progress and has at least shown some positive preliminary evidence of the utility of the dual-site catalyst. The researchers have accomplished some of their early milestones, but it is clear that they are still far away from their proposed go/no-go for Year 1.
- The project has made good progress toward catalyst synthesis and the demonstration of the peroxide sweeping effect. Initial demonstration of the thermal shock approach was not convincing and needs to be accomplished quickly or dropped.
- The team needs to confirm the atomic dispersion of metal, specifically Fe, in the Fe-N_4 structure. Fe nanoparticles are not strongly bonded to carbon. The performance of the atomically dispersed Fe catalyst meets the milestone (ΔE1/2 <65 mV versus Pt). MEA performance needs improvement (for both hydrogen–oxygen and hydrogen–air).
- While the project team is meeting some milestones, the project is behind on the more meaningful ones—thermal shock and even the catalyst development and scavenger milestones are lagging in momentum. The new materials made so far are both replicating others' approaches and performing poorly: P9 E1/2 <0.65 using zeolitic imidazolate framework (ZIF) materials is 150+ mV lower than several other groups, and 3.5% peroxide on the one catalyst with E1/2~0.8 (p10) is a huge peroxide level. The peroxide scavenging of Ta and Ce on slide 12 is clearly not meaningful for Ta and is only mildly effective for Ce. Similarly, on

slide 14, the Fe and Co Ta system peroxide reduction is questionable. Effective peroxide scavengers are well known in Pt systems, so it is unclear why new ones need to be developed. An acceleration in development and a down-select of thermal shock synthesis should be used quickly. The evaluation of the thermodynamics of active site formation should have been previously considered.

Question 3: Collaboration and coordination

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

- The project team has demonstrated a positive interaction between partners and has used ElectroCat resources to a satisfactory extent to this point.
- The project has balanced collaboration between academia (national laboratory and university) and industry.
- There was a strong collaboration with Ballard Power Systems, Inc.
- The team has established collaborations between different organizations.
- The initial collaboration has been focused on the thermal shock method. More explanation of why this approach is necessary and how it is scalable would be useful because it is not clear. The other collaborators should be able to contribute significantly to the project in the future and have complementary expertise.
- Good collaboration with ElectroCat is demonstrated and should be expanded. The roles of collaborators were not clearly enunciated during the presentation.
- The team has a good composition of national laboratories, industry, and universities. It would be helpful if contributions from each member could be identified through individual slides.
- Although rather unclear, collaboration seems to be ongoing.

Question 4: Relevance/potential impact

This project was rated **3.1** for its relevance to/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.

- The idea of incorporating a dual-site catalyst to improve durability by limiting radical-induced carbon corrosion is critical for any advancement of carbon-based, non-PGM catalysts. This project is very relevant to the goal of shifting away from PGM cathodes. For non-PGMs, durability is as important as activity; this is often overlooked. If successful, this will have a significant impact on the shift to non-PGMs.
- Catalyst performance and catalyst scale-up synthesis for MEA engineering and testing (50 cm^2) are realistic targets. MEA engineering for performance improvement in both hydrogen–oxygen and hydrogen–air is going to be the focus for the next year.
- PGM-free catalysts with improved activity and durability will lead to fundamental changes in the fuel cell industry.
- This project may have an important effect on reducing ambient peroxide generation in PGM-free catalysts, thereby improving durability. It is not clear how important a peroxide scavenger is in the catalyst layer as opposed to the membrane (where scavengers are typically incorporated), but this question can be addressed by this project.
- The project is relevant and has the potential to address degradation in PGM-free catalysts. To have higher confidence in the positive impact of the approach, the team needs to show the current versus time at a constant voltage in an MEA, with and without the peroxide decomposer.
- Peroxide scavenging is likely to be an important aspect of PGM-free deployment. However, the relevance of rapid thermal shock synthesis is less clear, as is scalability. It is unclear how this will be scaled, whether by lasers or a superhot fluidized zone or some other method. Arc heating thermal gradients are extreme, and the application to the carbon material used here seems extremely difficult.
- Non-PGM catalysts are a long-term and high-risk technology. It is too early to evaluate the relevance of a specific application, such as an automotive fuel cell. Non-PGM catalysts have the potential to be enablers for future products.
- The performance in MEAs was not demonstrated. A dramatic delay in approaching the first go/no-go decision could result in the inability to carry out this technology.

Question 5: Proposed future work

This project was rated **2.7** for its proposed future work.

- The general directions of the improvement area are acceptable.
- The proposed future work is well defined.
- The proposed future work addresses all of the potential issues, as well as what is required to successfully complete the project, but the team remains fairly vague on the work. At this point, the major hurdles include the low activity of the material and the molecular-level mixing of the two types of active sites. It is unclear how these will be addressed.
- The proposed collaboration with ElectroCat to demonstrate a material difference in durability using the consortium's newly developed active site degradation diagnostics could yield significant results. The team needs to report on a current-versus-time-at-constant-voltage test in an MEA, with and without the peroxide decomposer.
- While the future work listed is appropriate, there is insufficient detail to demonstrate how the current shortcomings will be overcome, especially with regard to the key thrust of thermal shock synthesis.
- The future work seemed broad and vague, without specific approaches enunciated. The most specific proposed future topic is the molecular-level integration of dual active sites. It is not clear how the project will accomplish this and whether it will have an impact on performance. It is uncertain whether peroxide is so tightly bound that an integrated catalyst will have more access to it than the current design. It is unclear how this can be demonstrated. A computational component is recommended.
- The proposed future plan was not correlated to the fact that the project team is critically behind on the performance targets established for the first go/no-go evaluation.
- Thermal shock activation should be hypothesized and verified in future work.

Project strengths:

- This is an important project to study the incorporation of peroxide scavenging in the electrode, as opposed to the membrane, and the team has made good progress in this regard by combining state-of-the-art electrocatalysts with effective scavengers. The project has a strong opportunity to improve on initial performance and demonstrate in an MEA with a comparison to scavengers integrated in a membrane.
- The project has decent ongoing collaborations and a world-class industrial leader in electrode and PGM-free development. A partial replication of PGM-free catalyst and peroxide scavenger development was achieved.
- The strength of this project is the project team's idea of incorporating dual active sites for the improved durability of the carbon matrix that makes up the catalyst. The preliminary evidence is encouraging.
- The team is pursuing a logical approach with the potential to improve PGM-free catalyst durability. The team has complementary capabilities.
- The project team is trying to explore some interesting ideas that are not currently being pursued by other groups.
- This is a strong team with a well-defined focus. This is a first-year review.
- This project's strengths include the materials synthesis and characterization.

Project weaknesses:

- There appears to be no clear plan to quantitatively understand the mechanism of scavenging and transport or the lifetime of peroxide throughout the MEA. Therefore, there are limited means with which to justify the integration effort and distinguish this approach from membrane-localized scavengers.
- This project is reinventing the wheel on catalyst and peroxide scavenger development and has not demonstrated good progress on either of these. Furthermore, the key original synthesis route is lagging and has been unsuccessful so far; the weaknesses and remediation of issues were not offered.
- The use of thermal shock needs to be removed and the funds reallocated appropriately. The key weakness of this project is the team's uncertainty in how to achieve molecular-level integration of the two types of active sites.

- There is a lack of chemical knowledge of thermal chemistry and the formation of active sites (for example, the role of zinc in synthesis). There is poor flexibility on the part of the principal investigator (PI) on making interim decisions and adjusting project objectives.
- More convincing evidence is necessary from an MEA test proving that the approach will improve durability.
- The catalyst performance is significantly behind other reports at the Hydrogen and Fuel Cells Program Annual Merit Review.
- Significant improvement in the MEA is a must for this project.

Recommendations for additions/deletions to project scope:

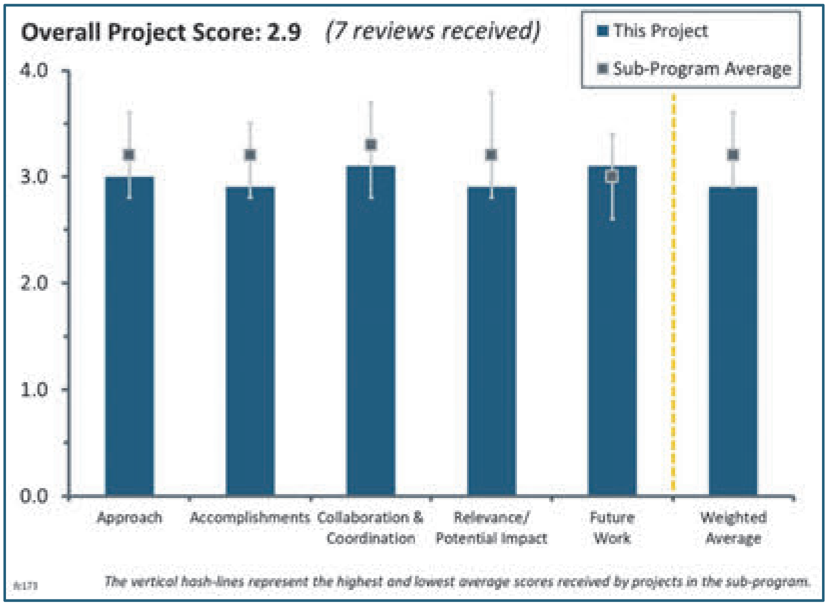
- It is recommended that the project team focus down to one thrust area, either thermal shock or peroxide scavenging, and evaluate meaningful metrics and milestones. If peroxide scavenging is chosen, the current approach is replicating well-established catalyst synthesis instead of developing something new. Similarly, for peroxide scavengers, it is unclear why the team does not use existing, more advanced approaches or even develop a completely new approach. If thermal shock is chosen, the team should evaluate the thermodynamics of approach and site stability quickly, and then evaluate the energy levels, controllability, and scalability of the different approaches—and create a quick go/no-go point. For example, it is unclear whether microwave synthesis can really achieve “shock” heating.
- A modeling component is recommended to follow kinetic mechanisms of ORR and degradation and to model peroxide concentration throughout the MEA. Also, an MEA diagnostic effort would effectively validate the model and justify design approaches. Unless the thermal shock approach can demonstrate clear near-term promise, dropping it from the project is recommended.
- It is recommended that the project establish a better understanding of N-hydrocarbon transformation and Zn removal from MOF during thermal shock activation. The PI should evaluate whether the team’s technique is more suitable to a precursor other than the MOF, perhaps for other nitrogen-containing organics.
- The project team should show that the thermal shock method is needed and scalable, or consider modifying that task. The team should also add a long-term MEA test showing improved durability at a constant voltage over time.
- It is recommended that the team remove thermal shock as a synthesis protocol and develop a defined procedure to address molecular-level mixing of the two active sites.
- Thermal shock activation should be well defined and hypothesized.

Project #FC-173: ElectroCat: Platinum-Group-Metal-Free Engineered Framework Nanostructure Catalysts

Prabhu Ganesan; Greenway Energy, LLC

Brief Summary of Project:

The project objective is to develop durable, highly active electrocatalysts for the oxygen reduction reaction (ORR) through a unique, bottom-up, rational design to enable a better understanding of the platinum-group-metal-free (PGM-free) active sites and improve activity. Fiscal year 2018 objectives include (1) developing high-throughput catalyst targeting porphyrinic and “phen”-type active sites, (2) exploring heteroatom doping, (3) beginning in-house membrane electrode assembly (MEA) optimization and fuel cell testing, and (4) positioning of the core laboratory ORR active site modeling with the experimental approach.



Question 1: Approach to performing the work

This project was rated **3.0** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The project’s approach entails rational synthesis to incorporate known functionalities of catalysts into high-surface-area microporous frameworks by tailoring pore size to optimize the catalyst–ionomer interface.
- The approach is promising; the team’s non-PGM cathode electrode demonstrated approximately 3–4 times less power density than current state-of-the-art (SOA) Pt/C cathodes.
- The use of porous N-containing organic frameworks provides a high-surface-area starting point for the synthesis that retains a large portion of the porosity and results in high-surface-area samples. Metal–organic-framework-based (MOF-based) materials have been shown to be effective precursors for active PGM-free catalysts. The team’s approach to try to control the number of N coordinating the metal (Fe) atom is noteworthy. The approach for the modeling efforts is useful. The work suggests a “bottom-up” synthesis approach, incorporating known functionalities into microporous frameworks to develop PGM-free catalysts; however, the approach is still relying on pyrolysis to obtain active materials. It is unclear what the structure of the pyrolyzed materials is and what remains of the “known functionalities.” It is not clear how the covalent triazine framework built from 4,4’ dicyanobiphenyl (DCBP) can result in a “phen”-type chelating framework. The geometry of the framework has too large of a spacing between the N atoms for one Fe atom to be chelated by bonding to two nitrogens in the framework. Bonding to only one nitrogen in the framework is not likely to result in a stable Fe species. The strategy appears to place an emphasis on controlling the number of N sites bound to the metal center (first backup slide correlating FeN_2 to activity), but the characterization and analysis of the pyrolyzed product so far has focused on identifying the type of N in the product and, to date, has not looked at determining the number of N coordinated to the metal center in the pyrolyzed catalyst. More characterization tied to determining the geometry at the metal center is necessary.
- The principal investigator (PI) will examine PGM-free catalysts based on porphyrinic polymers and “phen”-type chelating polymers. There are numerous approaches to create/optimize the properties of

catalysts, including reducing particle size, increasing the nitrogen content, and metallization. It is not entirely clear how the PI will prioritize these tasks.

- Using porous organic polymers as ORR catalyst precursors has its own advantages over other systems, as demonstrated in the literature. The approach emphasizes its “inherent chemical and thermal stability.” However, it is not clear where the stability advantage is since the same thermal activation is needed to convert the polymer to carbon.
- In terms of synthesizing and testing materials, the approach is good. The team is looking at a range of different precursor materials to achieve the highest possible activity. What is lacking is some definition and guidance to the approach. It looks like the project team is just feeling around in the dark, trying several different precursors and seeing what sticks. One of the major limitations of the specific focus on the precursor materials is the assumption that the final structure, N content, and degree of transition metal chelation can be controlled. The catalyst is synthesized by essentially burring in the precursors; it will never be possible to have direct specific control of that process. With that being said, insight could be gained through correlations, but that is better suited for a Basic Energy Sciences project than an Office of Energy Efficiency and Renewable Energy project. The project involves some computational analysis of the adsorption free energy of reaction intermediates on Fe-centered materials, but the connection to the experimental work is missing. It is hard to see how this is influencing the synthesis part of the project.
- The approach is aligned with the Electrocatalysis Consortium (ElectroCat) mission to improve PGM-free performance. It is not convincing that the technical approaches will be sufficient to address the durability of these materials.

Question 2: Accomplishments and progress

This project was rated **2.9** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- The project starts with a number of good polymer precursors with promising initial surface properties. Using a low-cost synthesis approach to porphyrin is helpful in reducing the PGM-free catalyst cost. However, catalyst performance needs to be improved, particularly for the “phen”-type system.
- The project began recently, on September 1, 2017, so the accomplishments have been modest. To date, the project team has completed Tasks 1.1, 1.2, 1.3, 1.8a, 1.8b, and 2.1. The synthesis of catalysts is progressing with some encouraging preliminary results—for example, the initial air performance of porphyrin-containing frameworks (as per slide 15), where the initial air performance is ~53 mA/cm^2 at 800 mV. There have also been some accomplishments regarding active site modeling, but it is unclear at the present time whether the model results will direct future experiments.
- The project team has shown some good results for a range of the precursor systems tested. Demonstrating the impact of Mn on the catalyst activity is promising. However, results from the computational work do not seem to be much different from previous results reported in the literature. Again, it is hard to see where the computational part fits in, as there is no apparent direct feedback to the synthesis.
- The project has obtained reasonable performance in an MEA in air for the brief period of time the project has been active. The project started less than a year ago. Characterization of the resulting materials is incomplete, and activity has not yet matched the current SOA for PGM-free materials.
- The project goals are not defined at full power, only at part power. The project’s full-power performance is approximately four times less power than that of current SOA Pt/C cathodes; it is not clear where the goal needs to be. For example, if overall stack cost is 40% Cath PGM and 60% balance of parts, then SOA stack costs are \$40 + \$60 = \$100. Supposing this project reduces cathode catalyst cost 10 times, the trade-off shows only half the power density. The new PGM-free cathode stack costs would be projected to be \$4 + \$120 = \$124. Thus, in this example, the total cost of the stack would have increased.
- The team’s approach should lead to higher active site density, which should improve catalyst mass activity. While the team still has until September to achieve MEA performance of >20 mA/cm^2 at 0.9 V, the current status seems significantly short of that. The other Year 1 milestones were not measurably challenging to achieve.
- The project team should optimize the synthesis protocol to prepare >400 mg of high-N-containing carbon-based materials per batch. More work is necessary to down-select polymeric materials for high-throughput synthesis.

Question 3: Collaboration and coordination

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

- The project team has developed good collaborations with good capabilities to evaluate the materials.
- There is good collaboration with partner institutions and an effective use of ElectroCat capabilities.
- This project has strong collaboration between industry and national laboratories.
- The project is a collaborative effort between Greenway Energy, Savannah River National Laboratory (SRNL), Northwestern University (NU), and Ballard Power System. No result/evidence was seen in the Hydrogen and Fuel Cells Program Annual Merit Review (AMR) presentation slides that the collaborators have made meaningful contributions. Collaboration tasks are listed in the AMR presentation. The project began less than nine months ago, so it may be too early to show results from team members other than Greenway Energy.
- There appears to be good collaboration between the modeling activities in this project and those at the Los Alamos National Laboratory. Collaboration between Greenway Energy and SRNL is going well. It is not clear what catalyst synthesis activities are being done at Greenway Energy and which are being done at other institutions (such as NU). It is not clear if Ballard has been involved yet.
- Greenway Energy and SRNL are in the same building, so the only funded external collaboration is with NU, whose polymer approach is complementary. Collaboration with other modeling and electrode optimization experts through ElectroCat may be useful.
- The presentation needs to identify individual member contributions clearly on the slides. It appears that the NU team has made a number of important MOFs and polymers, but this is not clearly identified in the presentation.

Question 4: Relevance/potential impact

This project was rated **2.9** for its relevance to/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 is a well-defined project. The synthesis of engineered frameworks should shift focus to the incorporation of Fe^{III} and Fe^{IV} sites. Experiments were designed based on predictions from density functional theory (DFT) models.
- The project is relevant, as PGM-free catalysts have a large potential impact on cost if performance comparable to Pt catalysts can be obtained.
- Using a porous polymer as a precursor represents an important route to PGM-free catalyst development.
- The exploration of new, inexpensive precursor materials is critical for further progress on these non-PGM materials. This project will be an important addition to the development of this class of catalytic material. While testing a range of precursor materials is necessary, a more fundamentally centered funding source is a better fit. This project must follow aggressive go/no-go decisions and down-selections to be competitive and relevant.
- Improving the active site density of the catalysts is an important effort. The project will not have much impact if the team cannot address durability as well. Fresh ideas for durability may be needed.
- The project meshes nicely with the ElectroCat program. There is a long-term need to reduce or eliminate the Pt content of fuel cell cathode ORR catalysts.
- It is not clear where the PGM-free full power targets need to be for automotive applications.

Question 5: Proposed future work

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

- The proposed future work is logical. The project is just getting to the point where results are coming in and strategies can be evaluated to see if adjustments need to be made to the original hypothesis.
- The proposed tasks are generally acceptable.

- The team's proposed future work is properly aligned to address the current limitations. One missing aspect from the future work is the assessment of material stability, in addition to activity. Both should be tested in parallel.
- The project team should optimize MEA fabrication to decrease high-frequency resistance and increase catalyst utilization; this is very important.
- The near-term future work should include some durability measurements on fuel cells.
- The direction of future work was unclear. There are several questions: how the experimental work will be prioritized, what perceived weaknesses in the catalyst will be addressed first, what will be optimized in the "phen"-type and porphyrinic-type catalysts, how many catalysts will be down-selected, whether rotating disk electrode data or fuel cell tests will be used to down-select, and how NU will contribute over the next year.
- The team needs to achieve activity targets and durability targets simultaneously. It is not clear that the approaches proposed will address durability. Improved active site density seems plausible with the proposed approach, but it still needs more work.

Project strengths:

- The project addresses an important subject—the development of highly active PGM-free ORR fuel cell catalyst powders. The project team is well qualified to carry out the proposed tasks. The PI has already collected preliminary data showing promising results.
- PGM-free cathodes have made a lot of progress over the past five years and offer the potential to address one of the biggest challenges for polymer electrolyte membrane fuel cells: PGM costs.
- The project's strengths include the identification of inexpensive precursor materials for the synthesis of active non-PGM catalysts. Another strength is the identification of the impact of mixed-metal centers.
- The team has an approach for increasing active site density, which should theoretically yield a much higher mass activity.
- The project has leading polymer synthesis experts helping to develop a PGM-free catalyst.
- One of the project's strengths is the attempt to control the M-N coordination number.
- This is a strong team and a well-defined project.

Project weaknesses:

- This project appears to be centered on a random survey of different precursor materials with tenuous guiding principles at best. It seems like the team is just gathering a few groups with experience and a few different precursor materials and trying things out. The approach needs to be more focused. The DFT analysis seems disconnected from the synthesis.
- Porphyrinic compounds have been examined in the past (e.g., by Yeager at Case Western Reserve University); that work ultimately failed. The stability of such compounds is still of concern. The team needs to focus on the ordering/prioritization of tasks to optimize the catalyst structure/composition/properties in future experiments.
- This is a first-year review, and more work should be done to optimize the catalyst to be successful by the end of the project.
- Mass activity is poorer than would be expected if there were more active sites. The approach may not address durability.
- Appropriate full-power targets should be stated and justified, and some durability data should be shown.
- The catalyst performance needs to be improved through better collaboration between the team members.
- Dicyanobiphenyl bipyridine (DCBP) geometry does not allow the chelation of metal by more than one N in the framework.

Recommendations for additions/deletions to project scope:

- It is recommended that the team provide more information about the range of conditions to be examined to optimize catalytic activity. The connection between the modeling results and experimental work needs to be strengthened. There needs to be more collaboration with national laboratories, Ballard, and NU.

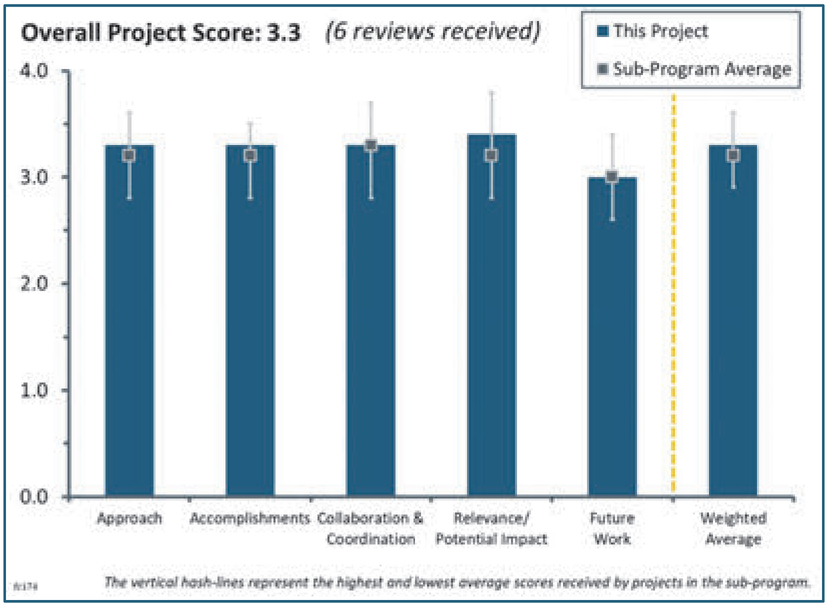
- Starting with DCBP and dicyanobipyridine (DCBPy), it is recommended that the team add additional nitrogen sources (small molecules) to adjust the M-N coordination number with these starting materials.
- Durability data should be demonstrated prior to optimization tasks.
- Durability and activity should be evaluated concurrently.
- Stability analysis needs to be added to the project.

Project #FC-174: Highly Efficient and Durable Cathode Catalyst with Ultralow Platinum Loading through Synergetic Platinum/Platinum-Group-Metal-Free Catalytic Interaction

Di-Jia Liu; Argonne National Laboratory

Brief Summary of Project:

The project objective is to develop ultralow-platinum@platinum-group-metal-free (PGM-free) nanofiber cathode catalysts that achieve all U.S. Department of Energy (DOE) fuel cell catalyst/membrane electrode assembly (MEA) performance metrics, particularly in the high current/power density region. The approach reduces platinum usage through synergistic interaction between ultralow-platinum and PGM-free sites by improving catalyst activity and durability/transport by using a porous nanofibrous network catalyst support instead of a conventional carbon support.



Question 1: Approach to performing the work

This project was rated **3.3** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- This low-platinum approach of low-platinum@PGM-free catalysts shows critical high activity in terms of rotating disk electrode (RDE) performance for an oxygen reduction reaction with PtCo on a calcinated Co metal–organic framework (MOF). Therefore, one of the 2025 technical targets (0.44 A/mg@0.9 V) on MEA performance has been easily passed. The project effectively shows the feasibility of low platinum loading at roughly 0.035 mg/cm^2 on the cathode, while the comparable performance to 2025 targets is still matched. The potential here lies in the better MEA performance with lower PGM loading than the DOE target of 0.125 mg/cm^2.
- The proposed approach is focused on the DOE Hydrogen and Fuel Cells Program (the Program) targets for reducing catalyst cost and improving durability and performance at high current densities. The technical approach is novel, well-thought-out, and feasible.
- Overall, this is a good approach, but it would benefit from the characterization of not just catalysts but also the carbon support/co-catalyst morphology and composition.
- The approach addresses all of the technical barriers and is technically sound.
- The approach calls for PGM loading to be very low on the cathode (<0.05 mg/cm^2), but higher loading with excellent power density may be an opportunity for lower grams of PGM per kilowatt and, therefore, an even lower-cost stack. A wider range of loading should be explored. If executed well, attempting to see whether active sites introduced by PGM-free materials could help to mitigate localized mass-transport losses at platinum particles would be a worthwhile approach. There is a high-current-density target in the project (1 W/cm^2) at the end. It may be preferred to have intermediate power density targets during the duration of the project. Electrospinning appears to offer the possibility of a catalyst preparation method that would be amenable to high-volume production, but the approach still leaves this unclear.
- The approach is a combination of electrospinning, PGM-free/stabilizing supports, and PGM-free catalysts. This is a promising approach, but the synergism claimed is not evident—and the possibility of platinum alloying with the residual base metals in the PGM-free support may be responsible for the observed

performance. Furthermore, the control case PtCo presented as a basis for claimed synergism is very poor, worse than pure platinum. Clarification on the actual approach materials and performance is necessary to keep the approach validity.

Question 2: Accomplishments and progress

This project was rated **3.3** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- Outstanding progress has been demonstrated toward the goals of the overall project and DOE. Targets on Pt mass activity and loss in performance at 0.8 A/cm^2 and 1.5 A/cm^2 are exceeded, while targets on MEA performance at 800 mV and 675 mV in air are closely approached. One of the biggest accomplishments of this project is the development of a complex catalyst structure that incorporates (1) a durable PtCo catalyst with a core–shell structure and (2) a catalytically active support that promotes the activity of the catalyst, enhances durability of the catalyst–support structure, and provides good transport conditions at high current densities.
- The project is on track, with strong work being done on catalysts and electrochemical characterization combined with modeling.
- The project team appears to have met initial targets based on the data presented. There needs to be some certainty reported about exactly what synergistic catalysis is taking place.
- Pt/C (BASF) baseline data is low for mass activity. The baseline mass activity should be near 100 A/g$_{PGM}$ (fuel cell testing). No indication was given of the different properties of PF-1, PF-2, PNNF-8, and PNNF-9. Since material differences appear to have substantial impact on mass activity, high-current-density performance, and the response to the electrocatalyst accelerated stress test (especially between PF-1 and PF-2), it would be interesting to understand how the different materials generate the differences in results. However, this is not shown. With 1.25 A/cm^2 at 0.6 V, a low grams-per-kilowatt result might be calculated, but without the anode loading, this remains unknown. Good durability in the electrocatalyst cycle is shown for LP@PF-1, but since there is little to describe the specifics of PF-1, it remains unknown why this durability was achieved. The presentation leaves uncertain whether all samples in the LP@PF series are PtCo. It appears that there is in situ alloying of Pt with Co in PF-2, but PF-1 is also of interest, given its durability. To be convinced of synergistic mechanism between PF-2 and PtCo, the presentation would have to indicate Pt loadings and PGM-free catalyst site densities or loading. There are a number of questions that could be asked regarding how active sites get preserved during electrocatalyst cycling. Whether the Co-N sites are preserved is worth studying. Mass activity could still be maintained (and peroxide could still be low) even after PGM-free sites are lost. The model needs validation with some simple glass cell experiments. It is unclear whether peroxide generation actually decreases with the presence of PtCo and PGM-free sites, more than it would with just the sum of these. This question still needs to be answered since the fuel cell data (without loadings or some normalized parameters) does not yet say this. Since the LP@PF-1 material was difficult to condition, there needs to be some understanding as to whether a highly durable material can be made that is also easy to condition.
- MEA performances at 800/675 mV and <40% durability loss on one of the best catalyst systems are still off from the goals. The weakness is related to the ultralow Pt loading on the PGM-free support (~3%). Such ultralow loading makes the oxygen transportation to the PtCo surface very difficult. The low backpressure (50 kPa) might also indicate the flooding issue on the relatively thick catalyst layer of the MEA. The increase of metal loading on the calcinated MOF might be critical to meeting all DOE goals. The density functional theory calculation indicates the formation and migration of H_2O_2 intermediate, which contradicts the observed 4e- process from the RDE. It is unclear whether the migration rate and the direction of H_2O_2 were taken into consideration. This is another weakness and is subject to improvement. Another question is whether this approach can be scaled up to the 50 cm^2 MEA level.
- The milestones selected are not very relevant to the work described—materials are made and characterized, rather than specific performance targets met. As such, the milestones should be adjusted to be in line with the Fuel Cell Consortium for Performance and Durability (FC-PAD) targets and guidelines. The tests conducted are not in line with the correct protocols for support durability. The benchmark consists of poor performance materials that are not even close to the state of the art (SOA), and no comparison is made to the materials known to be closest to meeting fuel cell performance goals.

Question 3: Collaboration and coordination

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

- This project is a well-coordinated effort between Argonne National Laboratory, Purdue University, and Northern Illinois University.
- This project leverages multiple partners that contribute significantly.
- This project's excellent collaboration is exemplified by Purdue University's contribution of modeling studies.
- An industry partner is suggested to test performance independently if the catalyst is further optimized.
- This is a small project so collaboration is harder. That said, the attribution to collaborators is unclear.
- It is almost impossible from the presentation to see what Northern Illinois is accomplishing. Purdue University is essentially working on a model that tells the project what it wants to hear. However, the model needs to be validated versus an electrochemical experiment. The project presents polarization curves that show LP@PF-2 performing much better than PF-2 or a PtCo/C catalyst. However, the Pt loadings are not shown, and the amount of PF-2 used is also not shown. Perhaps a combination of the PGM-containing and PGM-free materials were highly loaded to achieve the result, or perhaps the synergistic effect is true. However, it is difficult to see. Something from the Purdue University model should at least be directionally compared to something from fuel cell testing. The modeling collaboration could be much better integrated. The project is in sore need of a catalyst or catalyst-coated membrane supplier for collaboration. Otherwise, technology transfer is difficult.

Question 4: Relevance/potential impact

This project was rated **3.4** for its relevance to/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 helps to address the cost and performance of polymer electrolyte membrane fuel cells. It exceeds initial performance metrics and, if successful, will help push toward reducing the cost associated with fuel cell manufacture.
- This is a transformational project that is very important for the success of the Program; it has the potential for a significant impact on technology development.
- This project is highly relevant in combining low-PGM and precious-metal-free catalysts and demonstrating the synergy between these two approaches.
- The project has met most of DOE's 2025 targets in terms of MEA activity and durability on LP@PF-1. The remaining milestones have been proposed for future work.
- A new oxygen reduction catalyst that targets high power density and durability with very low PGM usage is relevant to overcoming the barriers of cost and durability in the Fuel Cell R&D sub-program. Despite the relevance of the project to technical targets, there is some concern over batch size. While the project may be using techniques that appear amenable to high-volume production (heat activation of MOFs, use of electrospinning, etc.), no data are presented to confirm that high-volume production can be achieved. The project's collaborators are all universities and national laboratories, which makes it difficult to see how scale-up will occur or whether anyone would be interested.
- The relevance is difficult to judge because the project does not align with the established test protocols and benchmarks outlined in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, and instead seems to be operating with little relevance to the SOA.

Question 5: Proposed future work

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

- The future work proposed is solid, so long as it follows established relevant test protocols, reports relevant benchmarks, and ensures that results are validated externally. FC-PAD seems like a likely and relevant validator.
- Future work is based on careful analysis of past progress. Future work contains a concise plan with clearly defined milestones.
- The proposed future work aligns well with the current work and is a logical progression. Scaling up the work done at the cell level to a short stack would be interesting.
- MEA studies must be the priority for these catalysts, but an “improved understanding” of the catalytic mechanism is essential for the project to have value. A microkinetic approach is recommended to validate the conjecture that the consumption of surface peroxide explains the synergistic effect, and especially to validate this claim in the MEA context.
- The principal investigator (PI) proposes to meet the remaining project tasks and milestones. Besides that, it is suggested the team improve the Pt loading, improve the mechanical integrity of the MEA, and demonstrate the scale-up capability. A better understanding of the synergistic effect of two active sites is also necessary.
- The project has a short time left, but it would do well to provide more convincing data on the synergistic effect and to achieve high-current-density targets. Future work indicates some of the former but will focus on current density at 0.8 V. There is no discussion of conditioning time in the future work, although this may be an issue for the most durable catalyst. There is a drive to achieve the lowest Pt loading possible. However, it is the best combination of loading and power density that provides for the lowest Pt content in a stack. The project needs to maintain this perspective.

Project strengths:

- The project proposes a novel approach for the design of low-PGM-supported catalysts that addresses several important issues simultaneously: catalyst activity, support durability, and the mass-transport properties of catalyst layers. The team has strong modeling capabilities that were successfully used to identify the synergistic interaction between the catalyst and the support as an important factor affecting catalyst activity.
- The project’s low-Pt design and SOA method have shown the potential of application. The approach addressed the key barriers with MEA testing slightly different from DOE target conditions. The team specifically achieved most DOE targets with quite low Pt loading at ~0.035 mg/cm^2 MEA. The MOF-based synthesis has the potential to improve the utilization of Pt in fuel cells. This project has strong technical expertise and avenues to achieve the remaining goals.
- The concept of using platinum with a PGM-free catalyst to mitigate local oxygen transport resistances is worth pursuing. The PI has a strong background with a particular class of PGM-free materials, namely MOFs. The power density and durability shown to date have been fairly impressive for some of the catalysts made.
- The project team has a specific set of targets and is hitting them well. There is good collaboration and a logical path forward.
- The project has strong catalyst and electrode characterization, as well as good collaboration on the modeling study.
- The underlying approach is promising.

Project weaknesses:

- An inappropriate reference was selected as a baseline for the comparison of results of fuel cell tests. The Pt/C MEA from BASF demonstrates SOA performance in neither a hydrogen–oxygen nor a hydrogen–air environment. Tail at high current densities is not usually observed at high current densities if SOA MEAs are tested under hydrogen–oxygen. PtCo-based SOA MEAs and catalysts need to be selected as a reference for comparison with the PtCo catalysts developed in the project, not Pt/C.

- The project team has not yet clearly demonstrated or modeled the synergistic effect that has been claimed. The project lacks collaboration with either a catalyst or catalyst-coated membrane supplier. The project also lacks fuel cell stack original equipment manufacturer guidance. This is evidenced by an insistence to achieve the lowest loading per area. The project team needs to further report on how material properties influence the resulting high current performance and durability.
- MEA performances at 800/675 mV and <40% durability loss on one of the best catalyst systems are still off from the goals. The weakness is the ultralow Pt loading of the catalysts, which allows the oxygen transportation issue to arise. The increase of metal loading on the catalyst might be critical to meeting all of the DOE goals. Another weakness is how to further explain the synergistic effect or prove its existence.
- Without relevant testing and comparison to the SOA, the true value is unclear. Furthermore, the overarching claim for synergism is unsupported.
- There seems to be some uncertainty in the synergistic reactions. A clear report on the reactions would be useful.

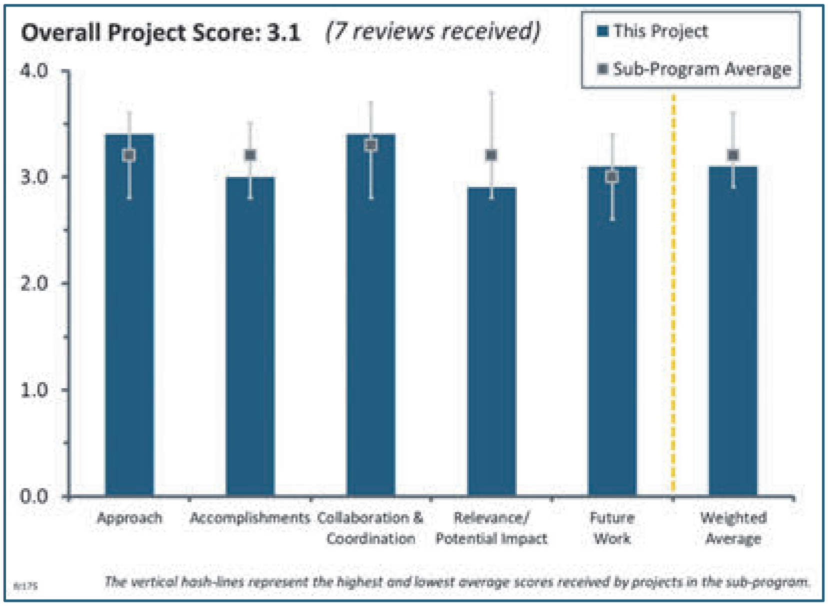
Recommendations for additions/deletions to project scope:

- No additions/deletions are recommended.
- The team should explore scaling up the work if the cell performance holds.
- Modeling needs to be shown to have a relationship with the experiments, or it should be removed from the project. The project should narrow its scope for the remaining time to show confirmation of the synergistic effect, achieve higher power density with a durable catalyst, and understand why catalyst durability exists. Some characterization should be done on active sites from PGM-free material after cycling. The conditioning time needs to be minimized.
- An MEA protocol is specifically needed for the MOF-based catalyst to maximize the performance, including durability.
- The project should be focused on relevant test protocols, appropriate benchmarks, and validation.

Project #FC-175: Polymer-Based Fuel Cells That Operate from 80°C–220°C

Yu Seung Kim; Los Alamos National Laboratory

Brief Summary of Project:



In high-temperature and low-relative-humidity fuel cell devices, one strategy to achieve cost savings is to eliminate or reduce the size of balance-of-plant (BOP) components, such as the humidifier and radiator. The objective of this project is to develop ion-pair coordinated polymers that can be used in fuel cells that operate at 80°C–220°C without humidification. The project is using density functional theory (DFT) modeling and small molecule study to determine the best candidate materials with strong ionic interactions. Membranes made of the selected materials will be manufactured, and the membranes' water tolerance and cell resistance in membrane electrode assemblies (MEAs) will be evaluated.

Question 1: Approach to performing the work

This project was rated **3.4** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- The approach of this project is great. It takes basic amines from the alkaline electrolyte membrane project and makes high-temperature proton conductors by reacting phosphate (H_2PO_4-) with quaternary amine and some added H_3PO_4 to get stable conductive and non-leachable membranes over a broad range of practical conditions.
- Starting with the DFT calculation before proceeding with the small molecule study was the right approach to determine the interaction between ammonium and phosphates. The MEA verification is the logical last step.
- The ongoing project phase with a limited duration of one and a half years investigates the feasibility of suitable ion-pair coordinated polymers regarding conductivity and water tolerance, and the team approaches this task well. However, with the key target and overall project goal of reducing the overall cost of the fuel cell system by using high-temperature polymer electrolyte membrane (HTPEM) fuel cell technology, special attention should be focused during the next possible project phases on:
    - Research on the feasibility of increasing power densities in hydrogen–air operation at reduced platinum loading to reduce overall cost.
    - The investigation of startup/shutdown procedures and the reduction of startup time. Startup/shutdown times have been one of the main reasons why HTPEM fuel cells have not been successful in automotive applications in the past
- Using an ion pair to enable the stability of a medium-temperature fuel cell system is a novel and creative approach. The concern is whether the polymer materials selected will be durable, as both have shown to be brittle at dry conditions. Also, over-potential losses due to phosphoric acid adsorption onto electrodes will likely always limit efficiency.
- The proposed approach appears very interesting and is based on new concepts of membranes.
- The first principle approach is good.

- This is an acceptable approach. There are barriers to these membranes that should perhaps be addressed, if within the scope. For example, swelling should be limited, and the team should address (or at least review) possible methods to reduce electrode poisoning from swelling.

Question 2: Accomplishments and progress

This project was rated **3.0** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- There has been great progress to date with the report of 0.8 W per cm^2 at 0.6 V at 200°C, and 200 W per cm^2 at 0.6 V at 120°C. The work also shows the possibility of running lower temperatures, such as 80°C, with the present membrane and claims of "proprietary membranes that have better performance and non-leaching ability." This is outstanding performance and durability for a fuel cell power source.
- Both the DFT calculation and small molecule study have been successfully accomplished and have achieved significant results. The MEA verification has been advanced significantly.
- Progress is good, based on the 18-month timeframe of the project and the focused scope.
- The project has met its go/no-go criteria.
- The results presented are encouraging. This new membrane leads to better performance than using HTPEM membranes but is far below state-of-the-art standard polymer electrolyte membrane fuel cells (PEMFCs), even with very high catalyst loadings. Durability is still unknown. Thus, much development is necessary to achieve DOE targets. In particular, the starting time and the performance below 80°C remain big challenges for the HTPEM fuel cells.
- There has been progress made in the identification of potential ion-pair coordinated polymers in the project. Initial testing results are looking promising, but significant additional work regarding durability testing, cold start, and catalyst loading reduction will be necessary in the next project phases to evaluate suitability for automotive applications.
- Encouraging power densities have been demonstrated, but pol curves were measured in oxygen (not air), with extremely high Pt loadings (approximately 10 times the PEMFC targets). Open circuit voltage (OCV) is ~800 mV, likely due to phosphoric acid adsorption, meaning drive cycle efficiencies are much too low. No plans were shown to address low OCV. The performance at lower temperatures is also quite poor, and there were no plans presented to address low-temperature performance, which would be a big problem during vehicle start-up.

Question 3: Collaboration and coordination

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

- The collaboration with Los Alamos National Laboratory (LANL), Sandia National Laboratories (SNL), Rensselaer Polytechnic Institute (RPI), National Institute of Advanced Industrial Science and Technology (NIAIST Korea), University of Stuttgart, NanoSonic, Inc., and Toyota Motor North America, Inc. hits all the bases for developing a HTPEM fuel cell for automotive applications. The main work consists of making and testing the polymer fuel cell at SNL and LANL, with good modeling and testing support by others.
- This project includes much collaboration with U.S. laboratories and international research teams; the work appears to be well coordinated by LANL.
- This project has good collaboration; LANL is getting polymers from RPI, University of Stuttgart, and SNL. NIAIST Korea is doing DFT work.
- The project team was well identified to attain, integrate, and test different structures.
- This project includes a balance of members from academia and industry.
- The project is a close collaboration with other research institutions and some support from industry. Industry involvement should be strengthened in the project.
- A wide array of other research institutes (including those from abroad) has been in cooperation for this project. However, the exact contribution of industry partners is unclear.

Question 4: Relevance/potential impact

This project was rated **2.9** for its relevance to/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.

- The project team has developed a high-powered (1 W per cm^2) HTPEM fuel cell. This may be DOE's "silver bullet" for making a practical fuel cell system with a minimum BOP. The BOP may be the most expensive part of the fuel cell, followed by the catalyst; using an HTPEM reduces the BOP, substantially offsetting catalyst cost plus raising the system efficiency on a well-to-wheel basis.
- The development of a high-temperature PEMFC membrane is of high relevance to achieving the DOE targets. If the performance and the durability achievements of the membrane are met, it will have a very high impact on the development of HTPEM fuel cells and on the transport applications.
- Addressing the fuel cell costs by improving fuel cell cost efficiency and performance by eliminating the BOP components, particularly the humidifier, is absolutely relevant and serves the goals of DOE.
- The current state of the art in automotive low-temperature fuel cells has improved significantly in the last few years. In some automotive fuel cell topologies, the humidifier has been removed; sufficient cooling, while still being an important development target, can be realized in common vehicle architectures. With this recent progress in low-temperature fuel cells, the benefits of high-temperature fuel cells should be reevaluated, and the team should carefully analyze whether cost targets (e.g., power-specific platinum loading, additional cost for high-temperature coolant loop) and performance targets regarding cold start capability and durability can be achieved. Strong industry support will be necessary to achieve a technology readiness level similar to low-temperature PEMFCs.
- The membrane alone cannot make the fuel cell into a high-temperature unit; catalysts and other materials are also necessary to work at such temperatures. Therefore, those particular perspectives are necessary to justify this project's focus.
- There are many, many barriers to this technology's working: membrane swelling, catalyst or catalyst ionomer-type poisoning, metal decay/agglomeration, electrode support corrosion, and low-temperature flooding. Phosphoric acid will slowly (and permanently) leave the MEA over thousands of hours. It is highly unlikely that the industry will address/solve these issues within the next 5–10 years.
- It is not clear that there is a push for higher-temperature fuel cells for automotive applications (as the project claims). The project's targets do not align with automotive requirements for power density, efficiency, cold start, or durability.

Question 5: Proposed future work

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

- After completion of the first project phase (the identification of feasible ion-pair coordinated polymers), the proposed technoeconomic analysis (TEA) should be performed as the next step to compare the potential of the high-temperature PEMFC with current state-of-the-art low-temperature PEMFC technology. With the higher operating temperature, alternative applications such as stationary combined heat and power might be considered, where the higher-temperature heat and the better contaminant compatibility (if coupled with a fuel processing system like a methane fuel processor) might provide additional benefit for high-temperature PEMFCs, compared to low-temperature PEMFCs, and might make the high-temperature fuel cells more attractive for these types of applications.
- This project ends soon, and the team has a good vision for more work. LANL and the members of the Toyota cooperative research and development agreement will work on electrode reactions. The team cites a need for electrode and membrane development and technology validation and scale-up. This project should be refunded and continued.
- The proposed work is in line with the short time remaining in the project.
- The proposed future work looks good.
- The only valuable future work is the hydrogen–air fuel cell testing and in situ water tolerance testing. Surprisingly, there did not seem to be any plan to down-select between the membrane and ionomer

concepts under evaluation. There is no planned future work focusing on improving OCV or low-temperature performance.

- Even though the ion-pair coordinated polymers have been shown to work fine as part of the project, a large number of substantial challenges remain (e.g., ionomer design and membrane development), each of which warrants its own project of large magnitude (i.e., these fuel cells seem far from commercialization).
- For fuel cell testing, other materials, such as catalyst and bipolar plate, should be identified.

Project strengths:

- The project's strengths include the systematic approach to reach the targets of the ongoing project phase. Progress has been achieved, considering the relatively short overall project duration. This project also has the involvement of several international research institutions.
- This project incorporates a creative approach of ion-pair interactions that seems to address the issue of acid loss in acid-base-interaction-based medium-temperature fuel cells.
- This project would have won the 2005 to 2009 "DOE HTPEM Competition" if it had been going on back then. The project has essentially overcome all of the barriers to a HTPEM fuel cell.
- The biggest strengths of the project are its high relevance, the remarkable progress that it has made, and the outstanding results that were achieved.
- A real strength of this project is its high level of domestic and international collaboration.
- This project has good work and focused goals.
- The strength of this project is material synthesis.

Project weaknesses:

- There is no particular weakness to underline, except the short duration of this kind of project (i.e., less than two years).
- With the further advancement of low-temperature PEMFC technology, some of the advantages of the high-temperature PEMFCs that motivated this project might have been reduced. This should be evaluated in a TEA as a next step.
- The project's weakness is its relevance to the industry. Success would greatly reduce BOP; however, multiple difficult and fundamental problems are in the way.
- The project does not address all of the critical requirements necessary for automotive applications, including efficiency and cold start. These may be critical flaws of this approach that are not addressed in this project.
- Many challenges still seem to remain for commercialization.
- This project needs more work.

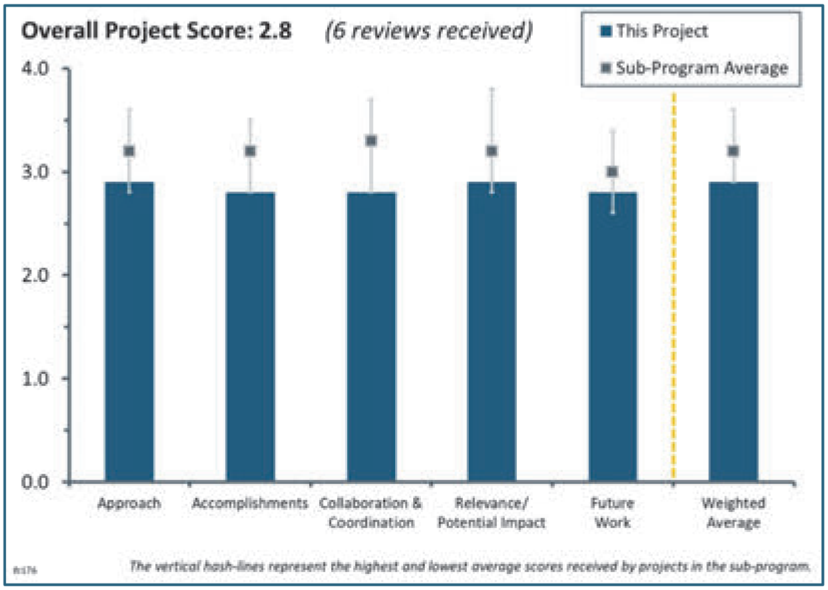
Recommendations for additions/deletions to project scope:

- As a next step, a TEA is recommended to compare the potential of high-temperature PEMFC technology with the current state-of-the-art low-temperature PEMFC development status. Platinum loading, durability, and start-up performance should be investigated.
- This project should prioritize addressing the low OCV in the fuel cell tests. The mechanisms should be understood and mitigation strategies developed. Otherwise, the efficiency will be well below automotive targets, and any other work on improving durability and reducing area-specific resistance would be moot.
- The project team should explain new "proprietary" membranes; that is, the team should address whether the membranes leach phosphoric acid when they perform at low temperatures—this is critical. A low-temperature startup or "cripple" mode would be excellent for a fuel cell power source. This project should be continued.
- The MEA and the total fuel cell material concept should be identified to justify this membrane development.
- It is recommended that the project team continue the investigation of the type of membranes.
- It is recommended that the team assess the metal dissolution rate at 160°C versus 120°C versus 80°C for the cathode.
- A deeper collaboration with industry partners seems desirable.

Project #FC-176: Fiscal Year 2017 Small Business Innovation Research (Phase II Release 1): Novel Hydrocarbon Ionomers for Durable Polymer Electrolyte Membranes

William Harrison; Nanosonic, Inc.

Brief Summary of Project:



Commercial polymer electrolyte membrane (PEM) technology is primarily based on expensive perfluorosulfonic acid ionomers. Hydrocarbon membranes represent a lower-cost alternative, but their utilization is currently limited because of their inferior performance and durability. This project is developing high-molecular-weight aromatic hydrocarbon membranes that possess polar moieties along the polymer backbone and pendant quaternary ammonium groups. This innovative chemistry will facilitate the fabrication of stable phosphoric-acid-doped ion-pair membranes for polymer electrolyte membrane fuel cells (PEMFCs) capable of 120°C operation for transportation applications.

Question 1: Approach to performing the work

This project was rated **2.9** for identifying and addressing barriers, project design, feasibility, and integration with other efforts.

- A novel membrane chemistry was proposed. The membrane composition is based on hydrocarbons (providing lower cost) with a sulfur group (providing improved durability due to the scavenging properties for hydrogen peroxide and radicals) and polar moieties (giving high conductivity and lowering the leaching rate of phosphoric acid, improving durability).
- This Small Business Innovation Research (SBIR) project is reasonably effective so far. The preliminary results are very interesting and have the potential to make some important contributions to overcoming some barriers facing the development of high-performance fuel cells.
- The project is fabricating stable phosphoric-acid-doped membranes to enable transportation PEMFCs to operate at 120°C.
- The synthesis of novel phosphoric-acid-containing polymers has relevance for potentially improving the performance of phosphoric-acid-based fuel cells. The choice of ammonia-group-containing polymers due to interactions between phosphate and ammonium offers some potential for improvement, particularly at very low water content. The primary limitations of phosphoric acid fuel cells—phosphate ion absorption and tolerance to liquid water—do not seem to be addressed.
- The focus on hydrocarbon polymers and the platform is an interesting approach, although these materials have been examined in the past. The focus on higher-temperature performance is important. The focus on structure/function properties makes for an important and good approach. The team should describe the scale of the current manufacture/fabrication and address whether the project will move toward roll-to-roll-type assemblies. It is unclear why phosphoric acid is being used instead of something similar imbibed with sulfuric acid.
- For the stated transportation application, while high-temperature (up to 120°C) performance is strongly desired, performance at low temperature (-30°C to 80°C) is paramount, as vehicles must start and perform adequately (meeting customer expectations) from ambient temperature. There does not appear to be a

viable path for this material set to provide acceptable performance in these conditions (which will include liquid water at lower temperatures, at least near a cell outlet). There are also questions as to the stability and durability of these materials at normal automotive and startup conditions (phosphoric acid leaching under wet conditions).

Question 2: Accomplishments and progress

This project was rated **2.8** for its accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals.

- This project has synthesized high-molecular-weight poly (thioether benzonitrile) copolymers with tailored compositions and tough films, with good thermo-oxidative stability. The team has demonstrated chloroacylation functionalization of copolymers and reaction conditions for reasonable reproducibility. The team has also fabricated quaternary ammonium-functionalized membranes and developed surface treatment for thin (<20 µm) and mechanically durable PEMs. The project team has demonstrated >150°C hydrated glass transition temperature of down-selected membranes, low dimensional changes (swelling), and good wet–dry cycling stability. Finally, the project has fabricated membrane electrode assemblies (MEAs) and showed stable conductivity over a wide range of temperatures and relative humidities (RHs).
- Membranes with a uniform thickness were synthesized and tested. For instance, membranes retain water at temperatures >120°C, are thermally stable up to 200°C, and have a glass transition temperature exceeding 150°C. Membrane mechanical properties were measured (tensile strength and elongation at break). The membranes resisted to a simplified dry–wet cycling version (25 cycles). Interestingly, the membranes were dimensionally stable in the in-plane direction, whereas a 50% change was noted in the through-plane direction. This anisotropy was not purposefully created, and it remains unexplained. The membrane conductivity is significantly better than Nafion under dry conditions in a temperature range of 80°C–200°C. Fuel cell tests have shown stable performance under dry conditions. However, performance is relatively low even with oxygen, rather than air, operation. From that standpoint, the fuel cell tests did not include specific measurements for the interfacial resistance between the membrane and catalyst layer ionomer. The proposed membrane chemistry is potentially amenable to solubilization to create catalyst inks, which would decrease the risk of a significant interfacial resistance. Several other key properties have not yet been measured, including oxygen and hydrogen permeability for both ionomer and membrane forms, and durability (i.e., resistance to hydrogen peroxide and radicals, dry–wet cycling over longer periods).
- Reasonable progress has been made in the synthesis of membranes and in evaluation of some membrane properties. However, more testing of the membranes under practical fuel cell operating conditions is necessary to confirm the claimed advantages of the proposed membranes—especially the long-term stability of the membrane. It is noted that Nanosonic, Inc. does not have the facilities for fuel cell testing; thus, closer collaborations with national laboratory partners are important to improving the rate of progress.
- The team has been successful in fabricating 20 µm membranes and has tested for conductivity, thermal stability, and mechanical strength. However, conductivity is far too low for transportation applications in which 0.1 S/cm or greater is required at operating temperatures between ~0°C and 80°C–100°C. If performance can be improved, the team will still need to demonstrate phosphoric acid stability.
- The work is fairly new and has shown new polymers and reasonable polymer performance. The group has shown improved performance in terms of membrane conductivity and has also shown reasonable phosphoric acid fuel cell performance. However, the results obtained to date do not suggest that these materials will replace current device materials.
- It is not clear whether the swelling and mechanical properties (e.g., pinhole formation and cracks in the membrane) are an issue or how they are being handled. Good progress is being made toward making the membrane thinner and less resistive. It is unclear whether the ionomer in the catalyst layer is being developed as well. The wet conditions in the MEA and whether there is liquid that is leaving the system for the imbibed system are both unaddressed, as are the peroxide testing and chemical accelerated stress tests. The team showed good results with the higher glass transition temperature (Tg) polymer chemistry, but it is unclear whether that limits the overall mechanical properties (brittleness) and the conductivity.

Question 3: Collaboration and coordination

This project was rated **2.8** for its collaboration and coordination with other institutions.

- For SBIR projects, collaborations tend to be more limited. The inclusion of Los Alamos National Laboratory (LANL) to do some of the fuel cell testing is an important accomplishment.
- The project team's collaboration seems good and appropriate.
- On a positive note, the team has engaged with LANL to develop MEAs for polarization curve testing. However, it is unclear whether analysis and learnings from these collaborations have been communicated. For example, the polarization curve (on slide 16) shows progressively reduced voltages at lower temperatures. High-frequency resistance (HFR) testing was presumably performed (if not, it should be) and would indicate if this reduction was solely due to lower conductivity at low temperatures or if it was limited due to flooding. This feedback is necessary for product improvement.
- Three partner organizations (U.S. Fuel Cell, Nissan North America, and LANL) were mentioned, but only one was clearly collaborating (LANL completed fuel cell tests).
- Some collaboration exists; however, coordination between partners could be significantly improved in the area of evaluation of high-temperature membranes in fuel cells under practical operating conditions. It is important to validate the claimed advantages of the proposed membranes in fuel cells under actual operating conditions.
- The fiscal year 2018 poster showed limited contribution from one partner and no contribution from other partners.

Question 4: Relevance/potential impact

This project was rated **2.9** for its relevance to/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.

- The commercial viability of fuel cell technology depends on (and is sensitive to) energy efficiency, durability, and cost. The operation of PEMFCs at higher temperatures could significantly increase energy efficiency and reduce the cost. Thus, if successful, the project has the potential to significantly advance progress toward the goals and objectives of the Hydrogen and Fuel Cells Program (the Program).
- The novel membrane has the potential to simultaneously reduce cost, improve durability, and have good ionic conductivity at high temperatures and low reactant stream relative humidities.
- The project is relevant to the Program's goals in that automotive stack operation at higher temperatures (up to 120°C) is desirable for extreme operating conditions (e.g., climbing a hill at a hot ambient temperature). However, more important is the performance (conductivity) at this high temperature, which requires 0.1 ohm/cm. Even more important is that this high conductivity is achievable over a broad range of temperatures and RHs, representative of real-world automotive fuel cell operation ranging from startup (-30°C–40°C), warmup (up to normal operating temperature, typically ~60°C), and normal operation (typically 60°C–90°C). This project appears to prioritize the high-temperature conditions without recognizing the imperative of the other, more typical, conditions.
- The project is relevant for moving toward higher-temperature performance, although there is still a question regarding whether the Fuel Cell Technologies Office and fuel cells should go in that direction. If successful, the project could have an impact, but issues related to polybenzimidazole (PBI) and the fact that it somewhat lacks commercialization are not seen as being overcome in this project.
- The measured membrane conductivity at 80°C is too low. Considering that the automotive fuel cells will spend the majority of lifetime at even lower temperatures, such as 60°C–70°C, this is a serious issue that must be addressed sooner rather than later. Perhaps the project should develop an accelerated test to demonstrate the long-term stability and retention of the phosphoric acid group under fuel cell operating conditions. The fuel cell performance with the fabricated MEA in hydrogen–oxygen is extremely poor. The performance will be even worse in hydrogen–air at reasonable stoichiometry and is unlikely to improve in humid environments. It is difficult to judge the cell performance without information on catalysts and Pt loadings.

- Phosphoric acid fuel cells have limited impact on many of the DOE's primary targets for performance and cost. Phosphoric acid systems have had limited impact commercially; this project tangentially addresses some of the performance issues that may have cost implications, but the work has nothing that makes a significant cost impact.

Question 5: Proposed future work

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

- The proposed future work is completely reasonable and offers potential for continued incremental improvements.
- The stated plans are sensible; future work will support layer investigation and the establishment of structure–property relationships. For automotive application, future work on the following is vital: improved conductivity at low temperatures, evaluation of material durability, and stability at low-temperature and high-RH (including liquid water) operating conditions. If the material can pass these tests, the project team should also work on operation under the DOE durability stress test protocols.
- Future work is commensurate with the project. It would be good to see more comparison to baseline PBI systems as well as state-of-the-art (SOA) fuel cell MEAs and membranes, beyond just conductivity. More mechanical compression is recommended, including perhaps looking at composite structures. Some focus on the ionomer should also be added, and the team should look at more fundamental issues of acid leaching, as well as how to mitigate those issues.
- Future work includes the use of a novel functionalized monomer, which would allow for greater ion-exchange capacity control during the membrane synthesis. However, the addition of a textile structural support to reduce cost remains unclear. How this support will reduce cost is unknown. Reactant permeability through the ionomer (for catalyst inks and reducing the interfacial resistance with the membrane) and membrane durability should be given higher priority. A more controllable synthesis and a lower-cost membrane are not useful if the ionomer and membrane do not have the potential to meet targets.
- The project team needs to place concerted effort on improving conductivity at lower temperatures, demonstrating the stability of the phosphoric acid group, and determining the causes of poor cell performance. The team should consider collaboration with system analysis experts to understand the limitations of this high-temperature membrane in automotive fuel cells and determine areas requiring improvement and focus.
- The outlined future plans are logical and built largely on past progress. However, more critical evaluation of the membranes and MEAs in actual fuel cells under practical operating conditions (e.g., subject to large current flow at high temperatures) is necessary to overcome some barriers.

Project strengths:

- The development of advanced high-temperature membranes is critical to the development of high-performance fuel cells. The proposed PEM has the potential to make an important impact on the development of high-temperature fuel cells. Some preliminary results to date are interesting, but further validation in fuel cells is necessary.
- The project has a good team, with the right capability and approach toward making higher-temperature membranes. Progress on conductivity and select membrane properties is good.
- In a relatively short development period, the project was able to demonstrate a thin membrane with some conductivity, strength, and thermal stability.
- The proposed membrane chemistry is novel and has the potential to simultaneously address key barriers (such as cost, performance, and durability).
- The project has a good, novel approach to an incremental materials advancement for phosphoric acid fuel cells.
- The project team has expertise in developing ionomers and fabricating high-temperature membranes.

Project weaknesses:

- Several key membrane properties (reactant permeability for both ionomer and membrane forms, interfacial resistance between ionomer and membrane, and durability) are currently missing, and therefore, a complete assessment cannot be finalized. Additionally, these aspects should be given a higher priority in future work. The contributions of two partner organizations are currently unclear. A data management plan is currently missing.
- Confirmation of the claimed advantages of the proposed membranes has yet to be demonstrated in fuel cells under practical operating conditions, especially for long-term durability. Closer collaboration with the fuel cell testing partner is necessary.
- The project team does not address, or does not comprehend, the full range of requirements and imperatives for an automotive fuel cell membrane (though the project may have some possible applicability to stationary power).
- More focus is necessary on mechanical properties, as well as transport. The ionomer and MEA and how these overcome existing SOA material issues seem uncertain.
- There is insufficient conductivity at low temperatures, and the long-term stability of the phosphoric acid group was not demonstrated. The cell performance was also poor.
- This project team did not take on water tolerance or the phosphate anion adsorption losses that tend to be major weaknesses and concerns for phosphoric acid fuel cells.

Recommendations for additions/deletions to project scope:

- For automotive applications, addressing the following is recommended: conductivity at low temperatures (-30°C–60°C), as well as the demonstration of stability and durability at these temperatures and under fully humidified conditions (including the presence of liquid water), including retention of the phosphoric acid sites. Upon successfully meeting the above, it is recommended that the team test to the DOE durability stress protocols.
- A broader materials space investigating more cation groups and/or tethering strategy could provide more fundamental information on the role of these cations in phosphoric acid retention and membrane properties.
- It is necessary to conduct more testing of PEMs and MEAs in fuel cells under practical operating conditions for a longer period of time (e.g., large current density at high temperatures).
- External collaboration with a systems analysis group is recommended.
- It is recommended that the team add compression and blister testing to the project.