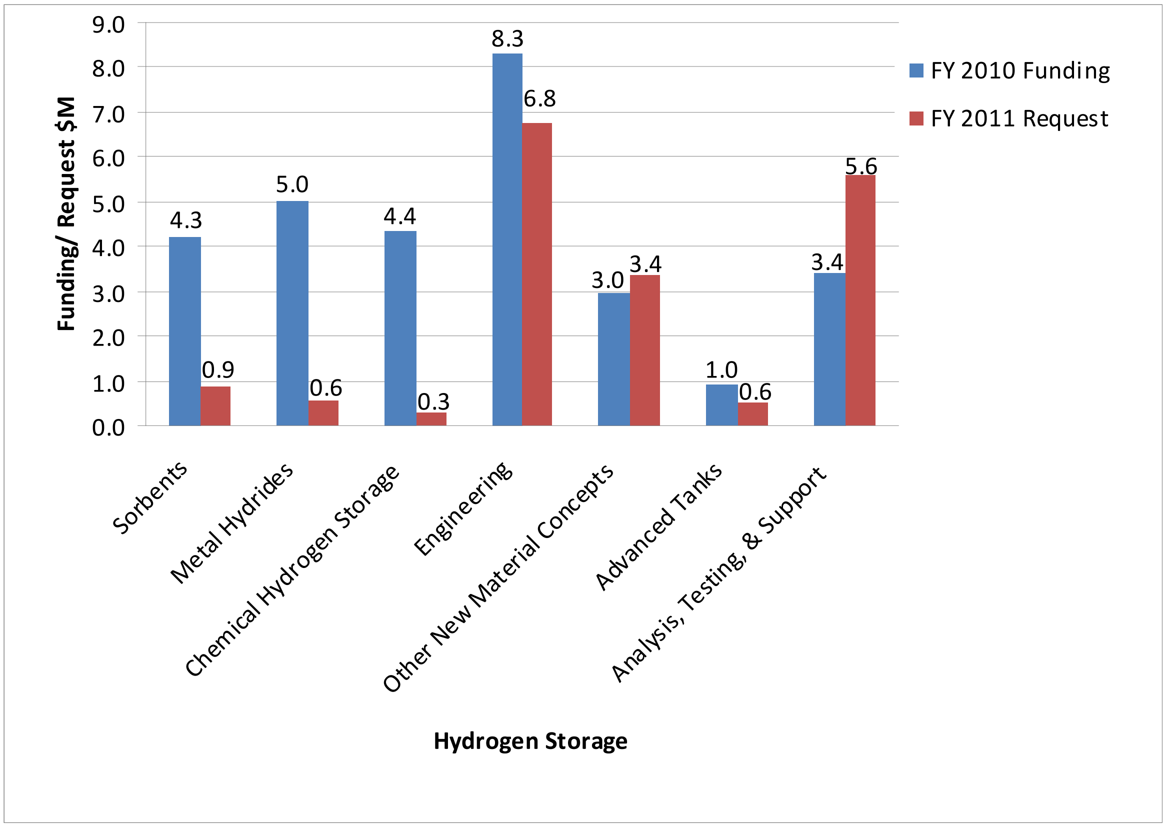
2010
Hydrogen Storage
Summary of Annual Merit Review of the Hydrogen Storage Sub-program

Summary of Reviewer Comments on Hydrogen Storage Sub-program:

The Hydrogen Storage sub-program portfolio remained focused in FY 2010 on materials based R&D and expanded efforts in system engineering for onboard transportation applications. The primary goal has been development and demonstration of commercially viable hydrogen storage technology to enable greater than 300-mile vehicle driving range, while meeting safety, vehicular packaging, and cost and performance requirements. R&D efforts remained focused on applied, target-oriented research of materials systems including high-capacity metal hydrides, chemical hydrogen storage carriers, and high-surface area adsorbents with the potential to meet the vehicular technical targets. In addition, the sub-program continued to support advances in physical storage (e.g., compressed hydrogen gas) for nearer-term applications.

Hydrogen Storage Funding by Technology:

The chart below illustrates the appropriated funding in FY 2010 and the FY 2011 request for each major activity. It should be noted that the three materials Centers of Excellence (CoEs) are scheduled to end in FY 2010.



Majority of Reviewer Comments and Recommendations:
The Storage portfolio was represented by 44 oral and 47 poster presentations in 2010. A total of 41 projects (29 presentations and 12 posters) were reviewed. In general, the reviewer scores for the storage projects were good, with scores of 3.9, 3.0 and 1.8 for the highest, average, and lowest scores, respectively. The projects were reviewed by three to eight reviewers each. Reviewers remarked favorably on the coordination and management of the Storage Materials CoEs. Key recommendations and major concerns for each project category are summarized below.

Chemical Hydrogen Storage: The goal of chemical hydrogen storage applied materials R&D is to develop materials with high hydrogen capacities from which hydrogen can be safely liberated at rates to meet vehicle powerplant requirements and develop energy efficient and cost effective pathways to rehydrogenate the materials. The general approach has been to use theory-guided experimental research to develop high capacity materials with favorable, ideally near thermoneutral, hydrogen release thermodynamics. Cost and energy efficiency analyses have been carried out on rehydrogenation pathways with the output used to guide improved processes. Other areas of investigation center on development of hydrogen release catalysts and strategies to minimize loss of volatile species along with the released hydrogen.

The Chemical Hydrogen Center of Excellence (CHCoE) has focused on use of ammonia borane and its derivatives as storage materials. Research is also being carried out within the CoE on liquid heterocyclic compounds that contain carbon, boron, and nitrogen (CBNs). For the CBN work, the reviewers found the idea of liquid phase storage materials favorable and they felt more effort is needed to understand the release mechanisms and limits to hydrogen capacity. In general, the reviewers found the CHCoE to be well organized and to have a strong collaborative effort.

Advanced Metal Hydrides: The overall goal of metal hydride materials applied research is to develop materials that can be charged with hydrogen on-board the vehicle at conditions amenable to the vehicle environment. Key barriers to this goal are the hydrogen charge and discharge kinetics at acceptable temperatures and pressures and the thermodynamics of the reactions which directly impact the net available capacity of the material. Metal hydride research within the Program has used theory to guide experimental efforts towards systems projected to be most favorable. One area where theory has lead to experiment is in predictions that particle size might be used to modify or “tune” thermodynamics. Progress has been made in designing and carrying out experiments to validate the projections on thermodynamics affects as well as to understand kinetic benefits to small metal hydride particles. New material discovery work has also continued with research on novel materials and use of unconventional solvents.

The DOE metal hydride research portfolio consists of projects carried out through the Metal Hydride Center of Excellence (MHCoE) and independent research programs. Overall the reviewers were favorable towards the metal hydride work. Coordination among the independent projects and with the MHCoE is recommended. The continued use of down-selections to eliminate efforts on material systems that do not show promise toward meeting targets and focus on systems that do is recommended.

Sorbent Materials: The goal of sorbent applied materials R&D is to develop materials with high hydrogen volumetric and gravimetric reversible net available capacities at closer to ambient temperature and at moderate pressure. “Net available” means that the temperature, pressure, thermodynamics, and transient delivery/uptake rates are taken into account to determine the amount of fuel available to the power plant. The general approach is to identify and design (often via theoretical modeling) high surface area per volume porous materials with increased hydrogen uptake capacities and higher binding energies for molecular hydrogen that will enable storage above cryogenic temperatures (e.g., higher than 77K, liquid nitrogen temperature). The key challenges have been to synthesize materials with high surface area per unit volume while retaining a narrow pore size distribution to maximize micropore over mesopore volume. As the hydrogen binding energy is increased using various strategies, the challenges then include achieving a “constant” heat of adsorption with coverage; then, as the binding energy further increases, challenges include issues with hydrogen uptake kinetics, net availability of hydrogen adsorbed, and thermal heat rejection upon refilling.

The DOE portfolio for sorbent materials has included the Hydrogen Sorption CoE and independent R&D projects. The reviewers noted that while many of these materials do show promise, issues still remain with achieving “net available” volumetric and gravimetric capacities and transient performance metrics that can meet DOE vehicular targets. Furthermore, retaining these properties at closer to ambient temperature/moderate pressure has proven difficult, as hydrogen/adsorbent site binding energies remain too low. In addition, external (to the research group) verification of excess capacity isotherms and isosteric heats of adsorption is recommended for all experimental groups. For many of these materials, additional characterization is recommended to complement the storage performance measurements such as NMR, neutron characterization to provide feedback into material design and verification data for the accompanying theoretical modeling efforts. Down selection of sorbents from further evaluation should be based upon criteria rooted in laboratory measurements, rather than upon theoretical predictions that had not been previously validated by experiments.

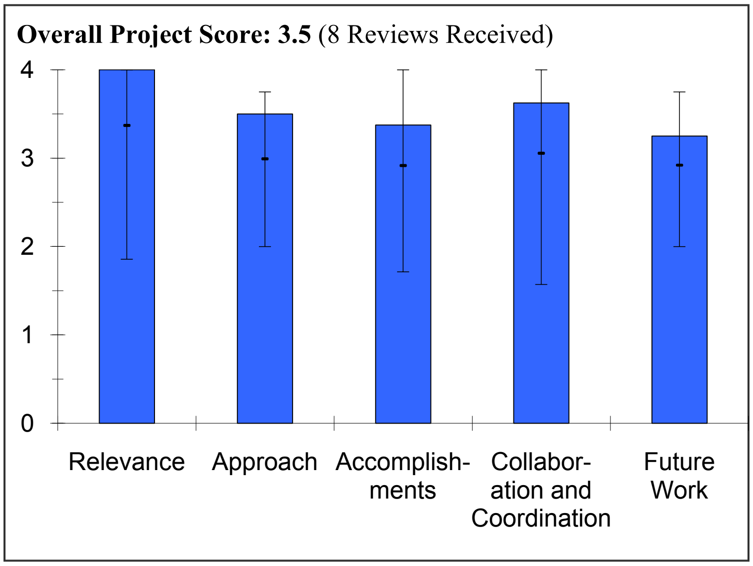
Engineering: Established in FY 2009, the Hydrogen Storage Engineering CoE (Engineering CoE) is a fourth CoE. The Engineering CoE comprises 10 partners and is led by Savannah River National Laboratory. The Engineering CoE is charged with developing complete system models and system designs for the three hydrogen storage material classes; evaluating the current state-of-the-art against the complete set of on-board vehicle hydrogen storage performance targets; identifying engineering R&D gaps and carrying out R&D to address the gaps. Phase III of the effort will include building and testing up to three complete sub-scale system prototypes for the material classes if sufficient criteria are met. Overall, the reviewers rated the Engineering CoE projects favorably. Concern has been expressed about the need for efficient coordination and communication between the Engineering CoE partners. It was noted that the matrix organization can be an effective structure if well managed and that certain partners appeared to have too diverse responsibilities or their activities were not thought to be in complete alignment with the Engineering CoE as a whole. Reviewers suggested that some restructuring and re-scoping may be necessary. Concern was also raised about potential scope creep, which needs to be carefully managed.

Advanced Tanks: The advanced tank R&D is conducted by a small but diverse group of researchers from industry, universities, and National Laboratories. A new effort this year, an investigation to reduce the cost of high-strength carbon fiber through use of melt-spin processing to reduce PAN precursor material, was highly rated by reviewers. Technical improvements in reducing the weight and volume of cryo-compressed tanks have continued, which could provide a pathway to meet the 2015 storage targets.

Analysis, Testing, and Support: The Analysis, Testing, and Support efforts provide independent verification of the potential of the various materials and technologies being developed through the sub-program. Performance and cost analyses efforts were completed on compressed and liquid hydrogen storage systems. The report, which will be publicly available, includes analyses of various options including Type III (metal liner) and Type IV (non-metal liner) cylinders and single versus multiple tank designs. The analysis efforts were also carried out to include the evaluation of the current cryo-compressed designs, indicating they have the potential to meet 2015 gravimetric and volumetric targets, and MOF-177 cryo-sorbents systems. Preliminary performance analysis of ammonia borane in ionic liquids was completed and a potential strategy to control the temperature of the exothermic hydrogen release proposed. Testing efforts include independent material testing to verify gravimetric and volumetric capacity claims. The reviewers felt these efforts were well executed and extremely beneficial to the Program.

Project # ST-01: System Level Analysis of Hydrogen Storage Options

Rajesh Ahluwalia; Argonne National Laboratory



Brief Summary of Project

The objectives of this project are to: 1) perform independent systems analysis for the DOE and to provide input for go/no-go decisions, 2) provide results to the Centers of Excellence (CoE) for assessment of performance targets and goals, addressing all aspects of on-board and off-board storage targets including capacity, charge and discharge rates, greenhouse gas emissions, and cost, 3) model and analyze various developmental hydrogen storage systems including on-board system analysis, off-board spent fuel regeneration efficiency, and reverse engineering, and 4) identify interface issues and opportunities and data needed for technology development.

Question 1: Relevance to overall DOE objectives

This project earned a score of **4.0** for its relevance to DOE objectives.

- The system analysis from this independent project is a healthy way of thinking and making decisions. This activity seems to work very well throughout the entire program.
- Argonne National Laboratory (ANL) is providing excellent systems analysis support to the Hydrogen Storage sub-program with respect to the assessment of various storage approaches compared to performance targets for light-duty vehicles. Their results provide important insights on the attributes and limitations of current configurations to meet technical and cost goals. This information is very useful for making go/no-go decisions on the continuation of the storage development projects.
- This project is vital to the success of the Hydrogen Storage Program. At this stage of the program, this project's comprehensive, system-level analysis is critical to proper assessment of different storage options, development of detailed performance and cost metrics, and a creation of a firm basis for go/no-go decisions. Results from ANL's analysis will undoubtedly be important for development of optimized systems by the Hydrogen Storage Engineering CoE (Engineering CoE).
- Having a good analysis is essential to the storage effort.
- ANL serves as an honest broker for this program.
- This project has always been highly relevant.
- This work is well-aligned and important for assessing the progression towards the DOE's RD&D objectives. Having a common analysis source of the various hydrogen storage systems is very helpful to ensure consistent assumptions.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- With various collaborators, it is possible to have appropriate input for modeling. Their approach is excellent.
- The ANL approach generally considers most, if not all, of the relevant technical parameters needed to assess the ability of a given storage system to meet both the on-board and off-board refueling performance targets. They collect and update input from various sources to obtain reasonably complete descriptions of several storage systems. Their analysis methodology seems to be thorough and sound

from an engineering perspective.

- The major limitation is the lack of sufficient details on specific properties of incompletely characterized systems (e.g., reliable rates for hydrogen reaction with the storage media in the appropriate operating temperatures). The consistent application of trade off studies to determine influence of various parameters is valuable to identify which have the most impact on achieving or limiting the performance targets.
- The team has adopted a solid approach that incorporates rigorous thermodynamic and kinetic models to understand important physical and chemical storage processes from a systems standpoint. Close collaboration with CoEs and other projects is ensuring that relevant issues are addressed. However, since the CoEs serve as the primary benefactors of these analyses, the dissolution of the centers in 2010 could dilute the overall impact of project in the future. A close collaboration with the Engineering CoE will be critical.
- Employing a systematic engineering approach by ANL ensures consistency across multiple storage solutions allowing for common-ground comparisons.
- ANL has done a good job of targeting the levels of analysis that provide relevant data but avoids complexity that would make modeling efforts convoluted and expensive.
- This project is scheduled for four additional years and requires a fair amount of materials information for the analyses to be viable, useful, and correct. With many materials projects coming to an end, how will this project acquire the input it needs to function appropriately?
- The overall approach is good. The recent analysis of attribute variations with the multiple tank system will be helpful.
- The validation of results and/or detailed explanation of assumptions should increase to promote confidence in the analysis. As indicated at the AMR, the analysis of the various storage systems are at different levels of maturity. It would be helpful to provide an indicator of the analysis level and/or confidence intervals for the results.
- The project team should be encouraged to provide details on their model approach.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.4** based on accomplishments.

- Significant progress has been made during the past year on updating assessments of physical storage
- systems, adsorption by metal-organic frameworks (MOF), and the ammonia borane (AB)/ionic liquid (IL) chemical hydrogen storage system.
- There are many case studies for various systems investigated under the hydrogen storage sub-program.
- ANL's project has been consistently a high performer. The rating here reflects the inevitablity of a reduction in resources for 2010.
- Their analyses indicate that while compressed gas storage can meet weight targets approximately and most of the functional targets, volumetric capacities cannot be achieved. On the other hand, their analyses of the cryocompressed storage vessels appear to confirm Lawrence Livermore National Laboratory (LLNL) results that nearly all on-board performance targets can be met. Yet well-to-tank (WTT) efficiency is impacted because of the need to form liquid hydrogen.
- The team presented a good, initial assessment of the on-board performance of AB/IL chemical hydrogen storage systems that indicated thermal management will be challenging for this approach. Overall, a broad range of systems have been evaluated by the ANL team.
- The team has made good progress on understanding important systems issues in compressed H_2 storage, cold gas/liquid storage, sorption using MOF-177, and storage in AB/IL systems. Results in 2010 on MOFs and AB represent a straightforward extension of work that was initiated in 2009 on these systems. Given the extensive work conducted on the AB/IL system, presenting a conclusion about the efficacy of this material in a complete storage system would be helpful.
- In chemical hydrogen storage systems, efficient rehydrogenation remains a serious challenge. Although this was addressed in a cursory way in 2009, a more focused effort on this problem is needed. Also, a detailed assessment of risks and identifying major obstacles to satisfactory system performance are not evident in the 2010 presentation. Quantitative risk analysis information is crucial for making well-reasoned, go/no-go decisions.
- The addition of fatigue analysis is a significant improvement on capabilities.
- Analysis corroboration of cryocompressed experimental results is a significant move forward for program.

- It would have been good to see better or more information comparing the different technologies as an outcome of the work to date.
- The results from this analysis shows the project continues to make excellent progress. It is very important to have an independent assessment of the various hydrogen storage technologies.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.6** for technology transfer and collaboration.

- There are various collaborators supporting this project. In particular, major industries are contributing critical analysis.ANL worked very closely with TIAX LLC on several storage systems. Apparently, there were close interactions and exchanges of information with the Metal Hydride (MH) and the Chemical Hydrogen Storage (CHS) CoEs that led to valuable feedback to all parties.
- There is a strong collaborative effort among ANL's SSAWG team and the other COEs and industry stakeholders. A wide range of systems issues is addressed. This is being successfully accomplished through a well-managed division of effort among the partners in the project.
- ANL has identified and established relationships with a wide range of partners to ensure it has the data needed for accurate analysis.
- They appear to be working closely with the Savannah River National Laboratory (SRNL) CoE consortium.
- This project makes a good effort to involve a significant number of collaboration partners. It would be helpful to ensure the collaboration partners are able to provide their feedback to the analysis.

Question 5: Approach to and relevance of proposed future research

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

- This project is expected to support the Hydorgen storage sub-program significantly.
- The immediate work is fairly clear. The more important questions are how to preserve the work done here and how to effectively leverage this work with the Engineering CoE's plans.
- The reviewer fully supports performing more comprehensive analyses of the compressed and cryocompressed storage vessels that include variations in design configurations and optimization that address manufacturing constraints for safety and structural materials (e.g., carbon fibers, aluminum versus stainless stell).
- Revision of the alane slurry system should only be done if more complete and update kinetics and composition results are available from Brookhaven National Laboratory (BNL).
- The fuel cycle efficiency of regeneration AlH_3, $LiAlH_4$, and AB are based on current schemes from the MHCoE and CHSCoE teams. On the other hand, there is little need for analyses by ANL for the on-board metal hydride or adsorption systems as this work should be done by the Hydrogen Storage Engineering CoE.
- Finally, the development of advanced concepts for organic liquid carriers would be of little value unless a real breakthough material is discovered since the energy efficiency is just too low for these higher temperature options.
- The future work is clearly stated, and it addresses important systems issues. However, the description of work on metal hydrides (e.g., reversible metal hydride storage system) does not provide sufficient detail to describe what will actually be addressed in future work on those materials. A forthright statement of obstacles and challenges plus mitigation strategies is needed. Close collaboration with the Engineering CoE should receive greater emphasis
- More detailed work on regeneration costs on alane or AB, for example, with an independent industrial validation of costs would be a good addition to this work. ANL should seek committment from an energy company to validate assumptions and methods.
- The future work plan for this project has the appropriate focus and continues to build on the progression of the past modeling progress.

Strengths and weaknesses

Strengths

- This project supports the entire hydrogen program.

- ANL has developed very comprehensive analytical tools for making a detailed engineering assessment of both the on-board and off-board aspects of hydrogen storage. Their results appear to be very reliable and robust from the current, comparisons-based knowledge and experience with available prototype and demonstration storage systems. The engineering staff is talented and industrious, and they provide clear presentations of their methods and results. Analyses are based upon best available data from their sources.
- This is a well-organized, comprehensive systems analysis effort that is being conducted by a highly qualified team. This effort is providing information that supports the entire hydrogen storage community on convergence toward an optimum storage material and overall system design. There is good communication between this project and the material COEs that has been vital to overall project success.
- The project team presented a high-quality, well-focused analysis.
- This analysis from a common source is key for comparing hydrogen storage technologies.
- The project involves the collection of input from a variety of sources.

Weaknesses

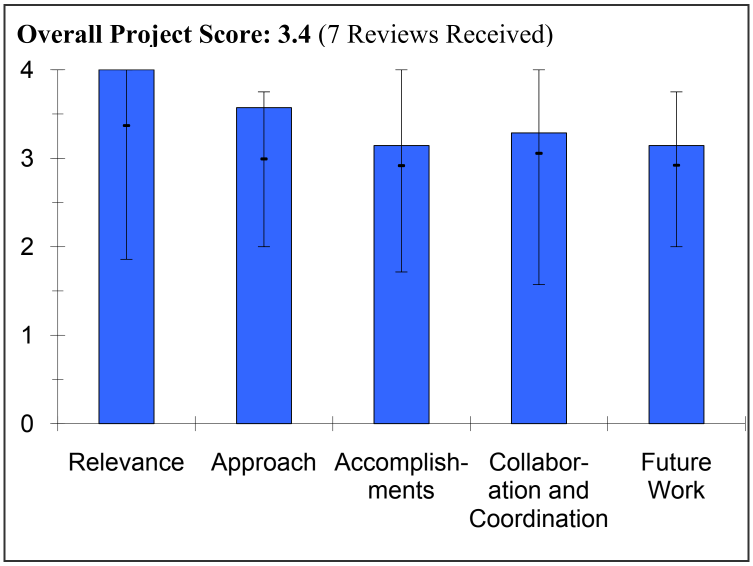
- There is a lot of output. Being indepth and precise is an issue.
- In general, system analyses are only as good as the correctness and completeness of the input data used by ANL. Often, ANL has had to resort to estimates and extrapolations or use potentially unreliable input parameters, as well as somewhat oversimplified storage system designs. Predicted system performance levels can be either too optimistic or pessimistic depending on the circumstances. Further work by ANL will probably be negatively affected by the absence of updated materials and properties due to the end of the materials CoEs contributions in 2010.
- A clear and definitive statement of obstacles and system challenges as well as mitigation strategies is needed for each of the approaches being investigated.
- The PI should be strongly encouraged to publish their analyses in archival journals.
- This information is too valuable to be lost in presentations that do not convey the whole picture. While it seems like the pace of publication has picked up somewhat, it is still far too slow.
- The project team should be encouraged to document the assumptions (i.e. archival reports) and validate the results.

Specific recommendations, additions, or deletions to the work scope

- This is an important project that has provided excellent analytical information for various storage options. It is recommended to preserve some aspect of this program within the Engineering CoE.
- A summary document should be developed detailing project results and providing overall guidelines for the storage system design.
- ANL should continue to focus on comprehensive assessments of the physical storage systems in configurations that can be used in vehicles in the near term and for early market applications. They should also emphasize analyses to optimize efficiency of the off-board aspects that are related to cryogenic/liquid
- hydrogen and regeneration of spent fuel from the various chemical hydride storage systems. ANL should minimize analyses of most on-board aspects of the three materials storage systems since this effort mainly belongs within the Engineering CoE. While some overlap is useful, duplication would be wasteful. Instead, the PIs should be strongly urged to foster more interaction, even outright collaboration, between ANL and the Engineering CoE to maximize information exchange.
- It is necessary for stronger emphasis on evaluating spent fuel regeneration schemes for chemical hydrogen storage materials including alane. A better connection and more collaboration with the Engineering CoE would be desirable as well.
- This project depends strongly on the CoEs to provide technical input and be the beneficiaries of the project results. Given the pending conclusion of the CoEs, it is unclear whether this project can operate as successfully as it has so far. A plan should be formulated to address this important issue.
- It is recommended they establish a partnership with an energy company to validate both monetary and energy regeneration costs.
- This project team and the Engineering CoE should establish a formal relationship to align assumptions and avoid duplicate analysis.

Project # ST-02: Analyses of Hydrogen Storage Materials and On-Board Systems

Stephen Lasher; TIAX LLC



Brief Summary of Project

The overall objective of this project is to help guide the DOE and developers toward promising R&D and commercialization pathways by evaluating the status of the various on-board hydrogen storage technologies on a consistent basis. Objectives are to: 1) evaluate or develop system-level designs for the on-board storage system to project bottom-up factory cost and weight and volume, and 2) evaluate or develop designs and cost inputs for the fuel cycle to project refueling cost and well-to-tank (WTT) energy use and greenhouse gas emissions.

Question 1: Relevance to overall DOE objectives

This project earned a score of **4.0** for its relevance to DOE objectives.

- This project estimates the costs for both the on-board and off-board aspects of large-scale (i.e., 500,000 units per year) manufacturing and operation of hydrogen storage systems. This information is significant to identify which proposed hydrogen storage methods has the potential to meet cost targets, if any. These analyses are based on detailed engineering information from Argonne National Laboratory (ANL) and other segments in the fuel cell and vehicles communities.
- The project is highly relevant and fully supports the DOE Hydrogen Program objectives. The cost and performance assessments being performed here are complementary to the storage materials development efforts within the material CoEs as well as in the Argonne National Laboratory (ANL) and Storage Systems Analysis Working Group (SSAWG) system-level analysis projects. Overall, it is providing important information that facilitates the evaluation of specific materials and systems approaches for on-board hydrogen storage.
- These analyses have been highly useful and relevant.
- The project is highly relevant and critical to the hydrogen program.
- A consistent and reliable cost comparison study is essential to gauge the commercial readiness of the program's multiple technology pathways.
- This project is highly relevant to the overall storage objectives because it concerns analysis of storage system cost. Until the Engineering CoE started participating, this project was the only source of rigorous system cost data. It is unfortunate that this project is coming to an end, since it has been invaluable for identifying and understanding cost-related barriers.
- This project provides an important assessment of the progression of various hydrogen storage systems toward the DOE RD&D objectives. It is helpful to have this analysis performed from a common source to ensure consistent assumptions.

Question 2: Approach to performing the research and development

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

- The TIAX approach is predominantly to use established cost analysis methods and tools based on engineering designs and manufacturing inputs from ANL, component vendors, and other sources. Costs are projected for large-scale production rates, which are subject to significant uncertainty for storage systems still in R&D development stages. The use of ranges for individual components and materials to determine the overall limits is good and is much more helpful than relying on just fixed design values. However, the analyses can be misleading for near-term, lower production rates and projected cost reductions by economies of scale when technologies are still being developed. The absence of reliable cost estimates for undeveloped materials can cause the TIAX results to be overly optimistic.

- The overall approach uses technology reviews and bottom-up modeling to calculate cost and performance for specific on- and off-board storage technologies. The approach is sound and provides an indication of the acceptability of different candidate technologies. The description of key design assumptions is an important component of the analysis, and it provides added credibility to the accuracy of the predictions.
- All the important factors and aspects have been taken into account.
- The study approach is sound and well established. The collaborative nature of seeking input from multiple partners is essential.
- Overall, the approach is well designed and focuses sharply on efficiently constructing cost models for diverse storage systems. The only area related to the approach that remains a bit unclear is how, or to what extent, the input information is vetted by technical experts and developers. Also, this approach has relied on extensive and frequent communications between TIAX and ANL, the creator of the system models and bill of materials. Given that ANL is frequently making changes to their models, it is unclear if all of these minor changes are captured in the corresponding TIAX cost models.
- The general approach is focused and effective. Even though cost models are difficult to validate, further explanation of assumptions and/or confirmation with industry partners could be provided to increase confidence in the analysis. Also, cost estimates at lower volumes would be very useful to assess potential of early-market commercialization.
- Although the project's title only names on-board hydrogen storage systems, the study presented results for both on-board and off-board hydrogen storage systems.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- During this project, TIAX has evaluated a number of hydrogen storage options in considerable detail.
- Their results seem mostly reasonable, although considerable extrapolation has been made from the current status of materials availability and processing. While there are differences in predicted costs, nearly all are very similar and well above the current DOE cost targets. Such studies are useful, but they do not directly lead to innovation or approaches that would significantly lower costs. One possible conclusion from these analyses is that no single storage option really provides a best cost alternative compared to the others. Improvement in the specifications of components and processing are apparent, but probably remain quite optimistic when compared to current status and costs.
- The 2010 effort is focusing on on-board assessments of MOF-177 sorbent materials and physical storage approaches. Solid progress was achieved on developing performance and cost metrics for systems comprising compressed and cry-compressed H_2, liquid-H_2, and MOF-177. Scale-up based on high-volume manufacturing considerations allowed predicted system performance and especially cost to be evaluated in the context of DOE targets. The high-volume manufacturing estimates assume 500,000 units per year. Although this is useful, it should be supplemented with estimates based on more realistic volumes appropriate for practical, near-term market entry.
- Since the project is now more than 90% complete, a more definitive statement about up-selected or recommended systems and approaches is needed. The project ultimately should provide input to DOE about the most highly recommended candidate among the storage systems evaluated.
- Their accomplishments and progress are very significant.
- The consistent and apples-to-apples cost comparison conducted by TIAX using the H2A model on a number of on- and off-board storage systems is valuable.
- The lack of reliable MOF-177 material cost, and even manufacturing capability, adds significant uncertainty to an otherwise impressive analysis.There needs to be a clear recommendation for the Engineering CoE or decision makers.
- The cost information for the updated MOF-based system will be very useful once the AX-21 (an activated carbon from Anderson Development Company) material placeholder cost is replaced with suitable MOF cost information data. While these updates are being made, other updates to the cost information for the MOF

system should be included – in particular, the newest ANL MOF system, which now operates at 150 bar rather than the original 250 bar operating pressure that ANL had first used.
- Also, the progress on well-to-wheels (WTW) performance is a bit unclear. These WTW energy efficiency values seem rather high and are more in-line with well-to-powerplant (WTP). For example, in the very optimistic scenario where we assume about 80% efficiency for production, about 95% for compression (e.g. 350 bar), and about 60% for fuel cell efficiency and neglecting delivery, the WTW efficiency for 350 bar would be approximately 45%, whereas the table presented lists 56%.
- The accomplishments from this project show they are making good progress in supporting the DOE's goals. There were several instances of using updated, previously performed analysis and, in general, a lot of recycled work.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- It is quite evident that the TIAX staff has worked very closely with ANL, Lawrence Livermore National Laboratory, Los Alamos National Laboratory , and others on many aspects of their assessments. TIAX has been responsive to design and configuration changes. TIAX also coordinated activities with the SSAWG members and DOE management with respect to areas of focus.
- Excellent collaboration among TIAX, ANL, the CoEs, and the SSAWG, especially in the area of WTT energy use and assessment of system life cycle issues. A well-formulated and executed division of effort among collaborators is evident. Good communication with stakeholders (e.g. the Freedom Cooperative Automotive Research (FreedomCAR) Hydrogen Storage Technology Team and other developers) aids in maintaining focus on the the most important issues.
- The project team has done an excellent job of interacting with the appropriate institutions to obtain accurate assessments.
- There appears to be a sound collaboration system in place for this project.
- It's not clear if there was a communication issue in one instance where the ANL team was not aware of TIAX's liquid hydrogen (LH_2) cost analysis results.
- It's not clear how TIAX's current proprietary cost model can be accessed by other PIs not part of the partnership.
- It is very unclear whether there are extensive collaborations with ANL and other partners. It is unclear to what extent this information is being efficiently shared with the Engineering CoE. Beyond the meetings and a final report, it would be very valuable if there were a formal process for TIAX and the Engineering CoE teams to interact and share information and ask questions.
- There appears to be a good number of collaboration partners involved in assessing this project. It would be helpful to ensure collaboration with an appropriate, cross-section hydrogen storage component and system suppliers to confirm the model assumptions. Only Quantum was referenced here.

Question 5: Approach to and relevance of proposed future research

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

- This is not applicable since the project is ending in September 2010.
- There needs to be an effort to preserve the work that this project has accomplished in the past few years. The transition and/or transfer of this project into the Engineering CoE would be beneficial to the hydrogen program.
- TIAX has proposed to perform and/or complete a number of analyses prior to the end of the project in September 2010. It is unlikely that it all can be done in the remaining few months especially with the departure of two key staff members working on this project. TIAX should focus on completing the physical storage materials assessments rather than try to estimate incompletely developed technologies such as alane or ammonia borane.
- The future work seems realistic for the limited period of performance that remains for this project. It will be critical for the TIAX team to offer compelling conclusions and definitive recommendations to the DOE, especially the Engineering CoE, on optimum system design(s) derived from this work. Cost analyses based on

moderate-volume manufacturing should be included to provide the DOE with cost estimates for near- and mid-term system deployment.
- The project ends in September 2010, but the future activities are very well structured.
- If it isn't already, a recommendation of the best hydrogen storage systems should be included in the final report.
- The project team should focus on completing the final reports instead of initiating new assessments this year, unless funding is extended for FY 11.
- They should prioritize findings and recommendations according to commercial readiness.
- As they mentioned in their presentation, making any and/or all updates – to the extent it is possible – to existing models is very valuable. More importantly, the culmination of all cost information and referenced assumptions in a final report is vital. The seamless transfer of this project's approach, tools, and learnings to the Engineering CoE, or other relevant projects, is imperative for this information to be efficiently used in the future.
- The next steps for this project appear to be aligned with the priorities of the analysis.

Strengths and weaknesses

Strengths

- Analyses by TIAX were closely coordinated with the engineering and design efforts by ANL and others. Both bottom- up and top-down scenarios were used to bound projected costs. Details of components and their costs were checked for feasibility when extrapolated to large-scale production levels.
- TIAX addressed off board issues with several technologies related to cryogenics and high pressure gas.
- TIAX also showed good flexibility in adapting its assessment to adhere to the changing priorities from the DOE's sponsors.
- The focused effort on cost analysis conducted in this project is crucial to optimizing the total storage system design. The TIAX team is well qualified to conduct this work; their results and conclusions could have an important bearing on the selection, development, and deployment of the most viable, near-term and far-term storage technologies.
- They made excellent independent assessments of various different types of hydrogen storage systems.
- The team presented a clear, consistent basis and assumptions of its cost analysis.
- The collaboration system is in place with key partners.
- This team is highly competent at cost modeling and has done an extremely good, efficient job taking system models from ANL and performing cost analysis for the systems.
- They exhibited very clear communication of information in presentations and making relevant comparisons to other storage technologies.
- This project is a common source of cost analysis for the various hydrogen storage technologies.

Weaknesses

- All cost estimates done by TIAX required extrapolation from current R&D activities and prototype or small-scale manufacturing volumes. Predicted costs can be unrealistic. For example, TIAX assumed that MOF-177 adsorbent would have the same materials cost as widely produced activated carbons during their assessment. Since precursors for MOF-177 are currently very expensive, it is highly unlikely that under any circumstance their costs be similar. The projected cost for hydrogen storage systems using MOF-177 is surely underestimated significantly. Even reliable cost estimates on any of the storage systems does not readily lead to a means to reduce the greatly over-target values. A close examination of technology hurdles and obstacles and how they affect the cost analyses is needed.
- There is a lack of clear prioritization and recommendation of storage systems, or showstoppers, for a given system.
- The analysis should include confidence levels for the cost estimates. The results appear to be absolute, but there is a different maturity of analysis for each system and for elements within the modeling such as purchased components.

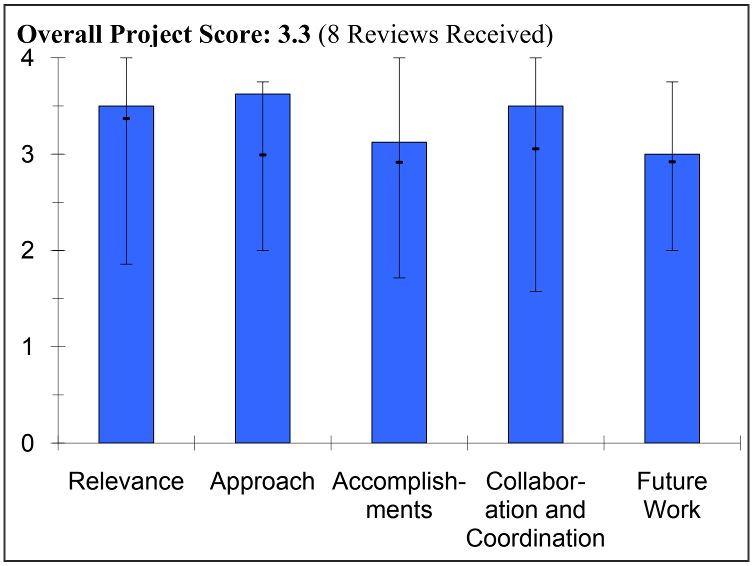
Specific recommendations and additions or deletions to the work scope

- This project has provided valuable analyses for many years. It is important to document a summary of the results and the methodology and assumptions used in the analyses.
- There needs to be an effort to preserve the work that this project has accomplished in the past few years.

- The transition and/or transfer of this project into the Engineering CoE would be beneficial to the hydrogen program.
- In the time left for this project, they should focus on on-board physical storage systems, such as compressed and cryocompressed/liquid, that could find near-term applications. In particular, they should assess the impact of much smaller production levels (i.e., hundreds to thousands per year) and alternative configurations. There is little to be gained from the incompletely defined chemical and hydride storage systems.
- A candid discussion of remaining technological hurdles and challenges for each of the technologies and how those challenges will, or might, be addressed would be useful. Although it would be difficult to do at this late stage in the project, a closer examination of alane system cost (especially spent fuel regeneration) would be informative. A more accurate assessment of MOF-177 cost is needed to properly assess the full-system cost. A cost estimate for volumes appropriate for the near- and mid-term market should be given in the final report.
- The project team should make their recommendations – good, bad, or ugly – based on current knowledge.
- See the comments on future work for scope additions in the remaining time.
- It would be helpful to have an additional estimate for each technology at a lower annual volume to assess the economies of scale.
- It is recommended to establish a formal relationship between those working on this project and the Engineering CoE to align assumptions and avoid duplicate analysis, for example, transfer of knowledge and model background.
- The project team needs to provide clear cost drivers for each technology to influence ANL system design.
- It is recommended to provide cost assessments at different capacity levels, instead of just 5.6 kg capacity level, since the cost ratio of dollars per kilowatt hour is not a linear relationship based on capacity.

Project # ST-03: Compact (L)H_2 Storage with Extended Dormancy in Cryogenic Pressure Vessels

Gene Berry; Lawrence Livermore National Laboratory



Brief Summary of Project

The overall objective of this project is to reduce or eliminate H_2 venting losses by researching vacuum stability, insulation, and para-ortho conversion. The objectives are to: 1) determine para-ortho effect on pressurization and venting losses, 2) directly measure para-ortho populations, 3) determine vessel heat transfer mechanism (radiation versus conduction), 4) evaluate vacuum stability by measuring pressure vessel outgassing, 5) test ultra-thin insulation for improved vessel volume performance, and 6) improve vessel design based on experimental results.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Hydrogen storage with sufficient volumetric and gravimetric densities for vehicular application at a lower cost is needed. Moreover, this is an original approach not pursued by others.
- This work is relevant to the Hydrogen Storage Program and DOE R&D objectives.
- Cryo-compressed hydrogen storage is a better alternative to compressed gas or liquid hydrogen storage.
- The project is relevant to the hydrogen program and the goals and objectives in the multi-year RD&D plan.
- This project directly addresses the crucial issue of on-board storage.
- The project is very relevant to the DOE program objectives. It offers a path to meeting the 2015 hydrogen storage targets.
- The reported gravimetric and volumetric densities of cryogenic hydrogen systems exceed the 2015 DOE targets. The project is attempting to optimize an actual H_2-storage vessel on board a real vehicle.
- Cryogenic H_2 storage systems are considered close to commercial reality, perhaps after the compressed gas vessel.
- Although the funding availability does not reflect it, the project is extremely relevant to the overall program objectives.
- The project is directed nicely toward the DOE goals with the appropriate emphasis on cryotank volume, weight, cost, and dormancy.
- The project has the appropriate overall focus on a high-density and low-cost hydrogen storage systems.

Question 2: Approach to performing the research and development

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

- It is difficult to improve this approach significantly. The project is progressing slowly but surely.
- One of the key issues is dormancy. This work aims to characterize two of the factors affecting dormancy with their studies of para-ortho conversion and vacuum stability.
- The project is focused on technical barriers such as volume, weight, cost, and hydrogen boil-off.
- The researchers have made continuous progress identifying the key needs to improve their system with minimal funding. Their work on identifying how the contribution of ortho-para conversion to extending dormancy helps to show the advantages of the system.

- The approach is good. The concept has been developed and refined for a number of years. Several iterations of the tank have been designed, fabricated, and tested. The analysis of the design and performance has been extensive. This year's effort was an attempt to reduce or eliminate venting by taking advantage of the para-ortho hydrogen conversion.
- The project's approach is sharply focused on developing compact, lightweight, and low-cost cryogenic on-board hydrogen storage systems.
- The project participants are looking at most of the critical variables in a logical and fairly complete manner.
- Their activities range from pure experimental such as para–ortho effects and insulation out-gassing, to modeling (CO_2 and cost calculations) associated with LH_2 manufacturing versus cryocompression.
- The approach with the analysis of para-ortho conversion and the benefit of dormancy was useful. Additional dormancy sensitivity studies would benefit the project such as variation in ambient conditions, initial states, and venting strategies. The project approach should expand on failure modes and noise factors that affect the system’s robustness like vacuum insulation lifetime variations.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- The project is following the initial plan.
- The project team has collected good data in monitoring para-ortho conversion.
- The PI showed the results of the cost analysis, but it is not clear how they arrived at the results. Because the analysis is sensitive to assumptions, models, etc., it is important to present the models used and the assumptions that go into the analysis.
- Their progress is good and concentrated on the following:
  - Composite out-gassing research that is necessary for establishing suitable getters for long-term vacuum stability;
  - Cycling vessels with cooled gas to separate mechanical and thermal effects without compression heating;
  - Out-gassing from vacuum-cured vessels with or without ultraviolet coating;
  - Attempting to acquire pressurized cryogenic H_2 fueling capability;
  - The focus of hydrogen liquefaction as energy and capital and intensive safety issues.
- The group has met 2015 targets.
- This project has produced a working system with weight and volumetric densities that exceed the projected capacities for any other system.
- There is no other hypothetical system close to this real, working tank.
- A lot was accomplished with very little funding in FY 10. Lawrence Livermore National Laboratory (LLNL) demonstrated that dormancy can be extended by a factor of two by taking advantage of the para-ortho conversion of hydrogen. There are issues that remain with vacuum integrity under automotive conditions. Out-gassing of hydrocarbons from the composite vessel will require an effective getter.
- This data may be the first on para-ortho hydrogen conversion in a full-size tank.
- The preliminary analysis of long term vacuum pressure data does not indicate increased heat transfer even at temperatures (140-240 K) nearing ambient.
- The project has clearly demonstrated its system optimization goal through para-ortho conversion and vacuum stability to minimize hydrogen loss and extending dormancy.
- The experimental results of the para-ortho conversion factor are impressive, especially in light of the low funding resource.
- Much progress has been made. There is at least one tank design (Generation 3) that meets the DOE 2015 weight and volume targets.
- The beneficial (endothermic) effect of the para-ortho conversion in increasing dormancy is nicely shown.
- The presentation dwelled excessively on the measurement details of this natural phenomenon.
- The out-gassing of the insulation and resulting decay of the vacuum and insulating properties of the vacuum space is sobering. It is unclear whether this is the principal remaining technical barrier at this point.
- The Generation 3 cyro-compressed pressure vessel appears to have made good progress and appears to reach the 2015 targets. The project should continue to focus on developing the counter points to cyro-hydrogen

disadvantages (i.e. energy penalty versus cost) and should avoid policy discussions involving carbonless energy premiums.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.5** for technology transfer and collaboration.

- There have been serious and active collaborations with original equipment manufacturer (OEMs) on the vehicular and the reservoir sides. There has also been excellent collaboration with the system analysis group.
- They have had frequent exchanges with BMW that was very helpful to the project.
- Collaboration with BMW and pressure vessel manufacturers to create a cooperative R&D agreement (Cooperative Research and Development Agreement, (CRADA)) will be helpful.
- Working with BMW is good. Unfortunately, the U.S. OEMs appear to be uinterested in this approach.
- Collaboration with BMW is key to demonstrating the viability of this technology in automobiles. Structural Composites, Inc., (SCI) will provide tank manufacturing expertise.
- The established CRADAs with an automaker and vessel manufacturer is the right direction for the project.
- There are two good collaborations: BMW and SCI.
- It seems there should be at least one more formal collaboration in the critical area of getter technology.
- The collaboration with BMW appears to be a good effort. Although, it would be useful to include and get feedback from cyro-system suppliers that could eventually produced these systems for OEMs.

Question 5: Approach to and relevance of proposed future research

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

- The project team focused mainly on finishing para-ortho experiments, filling with LH_2, designing fourth generation, and developing modular approach.
- Their proposed future work is fair.
- More understanding and data on para-ortho conversion is needed.
- The idea of using multiple volume vessels could significantly reduce the gravimetric and volumetric capacities.
- The proposed future work to explore performance limits of vessel and cryogenic hydrogen behavior related to shape, scale, refueling speed, and energy efficiency is good.
- The only negative here is the fact that the DOE has cut funding for this project.
- The DOE needs to increase funding for this effort to enable continued progress.
- The researchers appear eager to continue improving the system but have inadequate funding.
- A full automotive prototype tank will be built in 2011 by BMW. BMW indicated that they are developing an effective getter for compounds out-gassed by the composite pressure vessel.
- LLNL is not expecting DOE funds at least in the early part of fiscal year 2011, so future work plans are somewhat unsettled.
- The proposed future work is appropriate and necessary. However, the scope may need to match the funding level.
- The plans for future work are generally reasonable.
- It seems that relatively little continuing para-ortho measurement work is necessary to optimize the tank
- design.
- It is not at all clear how the optimum getter will be selected to handle the vacuum-jacket/out-gassing problem or whether LLNL have expertise in this area? During the Q&A session, a representative from BMW indicated a major effort was under way on the getter problem. He expressed confidence.
- The general explanation of future work seems to be clear and will build on their past progress. It may be worth including information regarding cycle robustness and degradation testing since this needs to be fully understood to gain confidence in this technology. The next steps regarding improving the out-gassing would also be very useful since this could be a significant item to develop the appropriate getter.

Strengths and weaknesses

Strengths

- It is a unique project generating lots of new knowledge. It may not be applicable for common vehicles, but many niche applications could benefit from the technology.
- They presented good experimental work.
- The PI has an excellent understanding of the problems concerning cryo-compressed systems.
- The institution and the PI bring good credentials for the proposed work.
- They have made great technical achievements, and have a good approach of blending fundamental understanding with real tank design and construction.
- H_2 liquefaction is energy intensive and costly, but total user energy and cost is what matters. LLNL estimates that the energy cost of H_2 liquefaction is outweighed by on-board storage and refueling savings with superior range and volume.
- LLNL made a case for lower user cost if a carbon premium from purchasing renewable electricity is assigned to the additional electricity needed for liquefaction when compared to compression.
- The project addresses practical, real-world engineering design challenges.
- The team has strong engineering and experimental capabilities.
- They have established collaboration with an automaker and a vessel manufacturer, which is beneficial.
- There is good scientific and engineering expertise on cryotank technology.
- LLNL has in-house ability to fabricate and test tank designs.
- The project strength is that the storage system attributes appear to be leading other technologies in the projections at this time.

Weaknesses

- There is a need for a well-to-wheel analysis and a clearer cost analysis.
- Materials issues need more focus that relate to fatigue, scale-down effect, types of fiber, and their overall affects on cost and safety.
- It is unclear if a liquid hydrogen fueling infrastructure will ever become widespread in the U.S.
- The volumetric efficiency decreases relative to tank capacity. The system looks more favorable for larger tanks.
- Customer preferences must be considered. Liquid hydrogen can result in a very inconsistent fill rate. There is also still the possibility of venting. These are things that can be overcome, but they are currently barriers.
- The discussion on carbon premium is unclear in the presentation.
- There were no weaknesses identified.
- They reported rather weak plans to solve the vacuum decay in the organics-containing insulation layer via getters.
- They are apparently relying heavily on BMW to solve the problem.
- The project needs to maintain an objective and non-bias view of the technology. This past year's effort has made progress in the area of providing data regarding the challenges and potential for cyro-compressed technology.

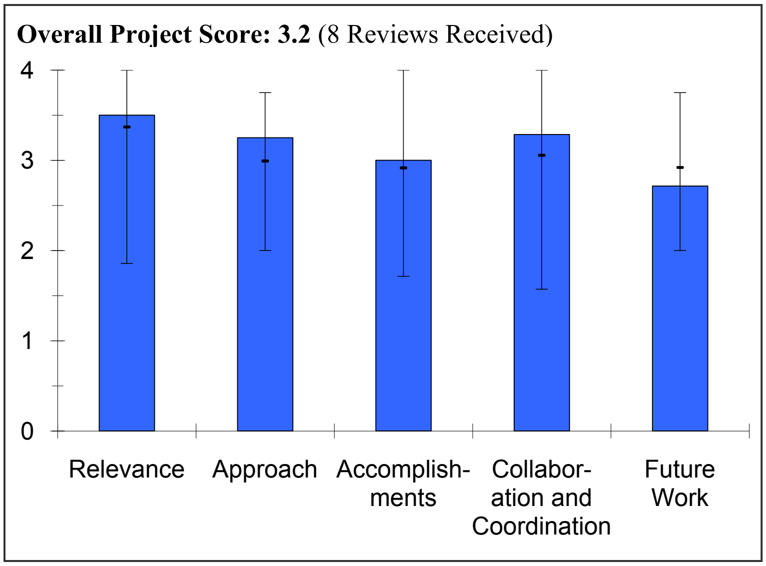
Specific recommendations and additions or deletions to the work scope

- The project should relate to available codes and standards for LH_2 and compressed gas vessels.
- They need increased funding. Let the researchers explore scaling for possible applications to buses and other large storage systems.
- Some funding should be made available at least to complete the development and testing of the automotive prototype tank.
- The project team should perhaps consider focusing their engineering design focus on potential early commercial applications, namely large heavy-duty vehicles , to take advantage of the lower unit cost of large storage vessel systems.
- The para-ortho measurements should be completed as soon as possible.
- Getter optimization should be a high priority.

- As mentioned an earlier section of this review, the scope should include a robust analysis of failure modes and noise factors that would influence the safety or performance of the system.
- In the scope of work, the team could consider approaches and suggestions developed for codes and standards organizations regarding validating a cyro-based storage system.

Project # ST-04: Hydrogen Storage Engineering Center of Excellence

Don Anton; Savannah River National Laboratory



Brief Summary of Project

The primary technical goals for this project are to: 1) quantify the requirements for condensed phase hydrogen storage systems for light-duty vehicle applications, 2) coordinate with all other DOE hydrogen storage programs to compile their media and systems requirements and data, 3) demonstrate the technologies required to achieve the DOE hydrogen storage 2015 goals, and 4) disseminate new design tools, methodologies, and components required to develop condensed phase hydrogen storage systems. The management goals are to: 1) effectively integrate the partner's required key technical activities, 2) facilitate their collaboration; and 3) interface with external stakeholders to communicate progress and transfer technology.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- The Hydrogen Storage Engineering Center of Excellence (Engineering CoE) is critical to the goals of the program to develop automotive capable H_2 storage systems.
  The engineering of hydrogen storage materials must be the first priority to realize the goal of the DOE Hydrogen Storage Program.
- The Engineering CoE represents the most tangible outcome of the entire hydrogen program. Not only it is one of the most relevant programs, the CoE is also a critical transitional step for the hydrogen program.
- When looking at the list of barriers addressed,it is hard to imagine that there is a deficiency of any kind in the degree to which the Engineering CoE will support the goals and objectives of DOE's hydrogen program. They are listed here:
  - A. System weight and volume.
  - B. System cost.
  - C. Efficiency.
  - D. Durability.
  - E. Charging and discharging rates.
  - G. Materials for construction.
  - H. Balance of Plant (BOP) components.
  - J. Thermal management.
  - K. System lifecycle assessment.
  - O. Hydrogen boil-off.
  - P. Understanding physi- and chemi-sorption.
  - S. By-product and spent material removal.
- The Engineering CoE is a broadly-based consortium that is addressing the critical issues impacting the successful development of an efficient and cost-effective condensed phase hydrogen storage system. The Engineering CoE draws extensively from completed and ongoing work by the other CoEs and independent storage projects. It directly supports DOE objectives and is a critical element in the overall DOE hydrogen program.

- The relevance of the Engineering CoE is questionable due to the fact that a viable material meeting program requirements has not yet been discovered. This is not a fault of the CoE but is related to work that preceded it.
- Because all of the hydrogen storage material CoEs have been terminated and none have found a suitable material that meets DOE targets for H_2 storage material, it is doubtful that the activities of Engineering CoE will generate any system-level success and therefore it is neither relevant nor critical to the overall DOE goals and targets set for the system-level, on-board H_2 storage.. The remaining money would be better spent on funding other worthwhile projects instead of continuing with the Engineering CoE..

Question 2: Approach to performing the research and development

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

- How does the effect of the materials centers shutting down affect the strategy of building 0-3 prototype storage systems? The materials centers have provided guidance as to what materials are ready to be handed over. This seems different compared to what the Engineering CoE is considering. A strong variable will be the availability of materials in large quantities. Perhaps the Engineering CoE should elaborate on whether these materials will be representative of future materials. There should be some kind of sensitivity toward the general material subsets and the effect on systems.
- The Engineering CoE is performing vehicle-level modeling, which is necessary to understand the interactions with the fuel cell and the vehicle to understand system buffer and startup requirements, etc, however the project team needs to be careful with the modeling approach..
- Next year, the CoE should do a better job of describing the inter-relationships of partners and why the particular work structure was selected since having many partners doing several tasks with the potential for mission creep for everybody and the overall coordination of tasks and responsibilities is somewhat confusing..
- The Phase I go/no-go requirement of having to meet a minimum of 40% of the targets across the board seems low. Original equipment manufacturers (OEMs) need to pick carefully to select the four target have to be 100% met. It is suggested that the project team selects targets that are least dependent on material properties or that can improve on previous tank work. Also, the targets need to be more engineering-based and not materials-based.
- It is questionable if the 100g size of the proposed prototypes will be reflective of full 4-6 kg-sized automotive systems. For instance will they accurately represent heat transfer, material compression and decreptition characteristics? It is understood that the systems are smaller because of the potential material availability and cost issues. The principal investigator (PI) should clearly describe these limitations and provide some kind of sensitivity analysis or projections of what larger systems will look like. A $40 million Engineering CoE should have the resources and capability to build full-scale systems. Richard Chahine at the University at Trois Rivieres has certainly built multi- kg sorbent-based systems, albeit not automotive ready.
  The funding and size of the prototype seem to be too small with only 15% of the budget will be spent on a 100-g scale prototype studies. Modeling is the major part of the project. There is much to learn from prototype studies.
- It could have been a discrepancy in the way different sub-programs have presented their work scopes, but it gave the impression that there are considerable redundancies. There appears to be multiple, parallel technical efforts in various areas of engineering design.
- It is not clear if there is duplicate work, since some of the work scope presentations were similar.
- Spider charts are a good way of measuring the state of readiness of each technology. For most long-term observers of the hydrogen program, the results are obvious. The question that was not addressed is: what pathway will make it to the prototyping stage?
- The institutions that were principal players in the Material-CoEs that started in 2005 have developed a keen sense of how to approach the issues that they unearthed during the preceding five years. The focus of effort is indeed sharp and to the point, seemingly in all respects. The organization of the Engineering CoE is all mapped out and in place, the roles and responsibilities have been spelled out, and the technical matrix approach looks like it will suit the Engineering CoE well. They used the spider graphs well. They track the whole development story for a given storage material type on one page. Also, the philosophy that go/no-go decisions require the Engineering CoE to consider and approach each of the DOE goals individually, and not concentrate only on one or two, is a good business approach.

- The approach is well formulated, and proven engineering analysis methodologies and strategies are being employed to quantify system requirements and demonstrate technologies capable of meeting the DOE system targets. The approach comprises contributions from Savannah River National Laboratory (SRNL) and partner organizations in all technology areas that are relevant to the evaluation of system design concepts and the demonstration of prototype systems. Assigning system "architects" to specific technology areas is a compelling approach to ensure that the Engineering CoE examines each technology in detail without ideas and concepts slipping throught the cracks.
- The project teams' focus on modeling coupled with experimentation is appropriate.
- Using matrix-based organization is a good fit for this CoE.
- Determining go/no-go based on targets doesn't mean a lot without cost targets. The DOE needs to provide cost targets as soon as possible. Materials regenerated off-board must include regeneration costs and forecourt costs, among others. To achieve this, the PIs may need to coordinate with other technical teams.
- The PIs have tried to map out the activity stream and required tasks and subtasks, despite the complexity of the project at hand. Non-material technology barriers have been identified satisfactorily. It is unclear how the lack of viable H_2 storage materials will affect the conclusions and deliverables of this CoE. It is also unclear why costing of the storage system was left out. Needless to say, cost plays a major role in choosing among the different designs and system approaches. Another issue is that the Engineering CoE managers have not clearly identified which four of the DOE 2010 numerical system storage targets will be met by the first go/no-go decision point. Also, it is not certain which six of the DOE 2015 numerical targets will be satisfied by the second go/no-go time, and it is unknown why cost is not one of the decision criteria considered.
- An integrated team and approach are crucial success factors for this CoE.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- The CoE has progressed well in a year with most of the effort focused on modeling. Go/no-go criteria and the decision tree for what and/or how many systems will be constructed should be provided.
- There have been a lot of results but depth of the PIs' consideration is a question mark. For example, it is unclear whether the comparison of sorbents to determine whether they are commercially available was really needed.
- The program is still in its early stages. The subprojects have already provided valuable information. However, a large portion of the results presented here appear to be duplicates of earlier projects. It would have been helpful to delineate from the original work done here versus previously performed prior work.
- In reality, the project is better than good, perhaps a rating of 3+ on this metric. The results portion of the presentation is, in its present stage, a floor plan for what is to come. Work is just underway on most tasks, so progress is hard to gauge. It is fair to say that the early results, where there are results, look promising. It is anticipated that progress in the coming year will be significant in several areas.
- Solid technical progress was achieved in four of the six technology focus areas – the project is off to a good start. However, the presentation of accomplishments in the Multiple Model Level Coordination task and the Storage System Modeling task lacked sufficient detail to allow a reasonable review. The spider charts derived from the system analyses provide an excellent means to communicate the results in a concise and understandable way to the reviewers and technology community. The charts also are used to highlight problem areas where additional resources and technical efforts are required.
- This project was good for the first year.
- The acceptability envelope is a good tool. It would have been good to have seen results for various materials.
- Now, more than a year through the life of the Engineering CoE, the CoE still appears to be in flux and the accomplishments presented were limited. This is not surprising in the light of the complexity of the whole operation.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- There is good collaboration with the key partners that have built systems in the past. It is critical that the OEMs remain engaged, particularly on vehicle-level modeling and in providing key performance metrics that the CoE must consider and understand for automotive designs.
- There are three materials CoEs but only two are involved in the Engineering CoE as collaborators. Modeling is important but it is not a magic technology. Both experimental and modeling work with real materials is indispensable for the Engineering CoE to learn from.
- The Engineering CoE could benefit greatly by developing some form of collaborative work with Argonne National Laboratory (ANL) and TIAX LLC system analysis projects. It is imperative to maintain the institutional memory and build on previous experiences.
- As the last remaining CoE, the Engineering CoE has the added responsibility to maintain and preserve the institutional memory of the entire Hydrogen Storage Program. The current level of interaction and specific leveraging of the other centers are not adequate. This is an organizational gap that the DOE managers must address.
- The leadership of this project has done an excellent job of pulling together its diverse portfolio of partners, defining roles and responsibilities, and getting collaborative research under way in the past year. The plan for intra-center communications is certainly adequate. It remains to be seen how things will go with the extra communications.
- They have excellent collaborations, and cooperation among participating partners are evident. There is good division of work effort among all partners. A serious management challenge with a project of this size and scope will be the ability to effectively perform rapid mid-course corrections in a way that doesn’t totally disrupt project flow.
- They exhibit good coordination and communications with partners.
- There are many entities involved – perhaps too many. It is not clear how closely these groups are working together. There was no example of close collaboration that resulted in a tangible result given that which otherwise could not have been possible. A few months before the first go/no-go decision deadline in October of this year, Engineering CoE PIs needed to present solid progress toward meeting the DOE system-level hydrogen storage targets.

Question 5: Approach to and relevance of proposed future research

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

- They critically need input from a materials CoE. One of the original intents and benefits of the Engineering CoE was to provide clear feedback to the materials CoEs and its scientists to better guide them in the development of materials. It is strongly recommend that the remaining independent material programs be aggregated into some kind of a materials CoE to maintain this critical information link between materials and engineering considerations
- Modeling is important but it is not a magic technology. Results from materials work and investigation of prototypes in more detail on a much larger scale is indispensable.
- The future plans for this project do clearly build on past progress, albeit mostly from the findings of the Materials-CoEs, and are sharply focused on critical technical barriers. The individual Engineering CoE partner presentations more details about future Engineering CoE plans at a task-by-task level than did the Engineering CoE overview presentation.
- The future work is a straightforward and appropriate extension of the current work already underway. It is keenly focused on addressing important engineering obstacles and issues. The major challenge in the coming years will be the integration of engineering solutions with materials that have properties that are marginal in terms of the DOE goals and objectives.
- The project needs quick incorporation of costs even without targets.
- They need to clearly define the benefits of prototyping systems for materials whose performance is far below target values for critical targets.
- It would be good to have a better understanding of proposed outcomes, such as proof of concept systems and prototypes that will be the outcomes of the work.
- The proposed future work to achieve the level of progress needed to pass the first go/no-go decision point ties with achieving four of the DOE 2010 numerical system storage targets. The remaining numerical targets having met at least 40% (an arbitrary target) or higher of the DOE target misses the no-cost data being compiled and

the no-cost targets are set. None of the materials advanced to tier one are able to furnish a system-level device capable of meeting DOE near- and long-term numerical hydrogen storage system targets.

Strengths and weaknesses

Strengths

- Engineering is key to realizing the hydrogen economy without doubt.
- This is a very strong technical team.
- OEM participation is a strength.
- The accumulated knowledge and insight of the participating institutions and individuals concerning the subject matter of this project are outstanding. The participants have engaged this project with comprehensive understanding of the issues, barriers, targets, and overall goals.
- The knowledge, data, insights, tools, and techniques developed during the years of the Material-CoEs are at the disposal of this project. The foundation for beginning the work of this project is well established.
- This is an exceptionally well-qualified team who are well organized and managed. The team is addressing a broad set of engineering challenges in the development of an on-board storage system in a timely and comprehensive way.
- This is a strong team.
- They exhibit good organization.
- Communications appear to be working well.
- A large number of well-qualified researchers and scientists are involved in this Engineering CoE.

Weaknesses

- One of materials CoE is not officially included in the activities of the Engineering CoE. [DOE note: liassons exist between the Engineering CoE and all 3 of the ending Materials CoEs, addtionally Engineering CoE partners include partners from each of the 3 Materials CoEs]
- The major activities are modeling, not prototype testing.
- The safety issues and codes and standards are not included and even collaboration on these activities were not presented at all.
- There are too many redundancies in the technical area.
- They need to develop a more organic transition from ANL and TIAX to the CoE.
- The project leaders should make an effort to prioritize their goals and objectives. Even though there is a sense that every task area is critical, the program must be prepared to deal with the prospects of budget uncertainties that are likely to plague DOE programs in the coming years. The present administration balances the funding of energy research against the need to reduce federal deficits.
- It seems that from a hydrogen program standpoint, the output of this CoE will be the final, and arguably the most important, contribution to the overall program. However, to date, no single material has the necessary thermodynamic and kinetic properties or the volumetric and gravimetric capacity characteristics to satisfy DOE goals. The excellent work on system engineering being performed by this CoE, notwithstanding, seems unlikely to produce a final system solution that meets DOE goals without additional materials development. With the dissolution of the material CoEs, a serious concern going forward is that the Engineering CoE will be limited to examining only materials with limited or not fully-tested storage characteristics that are currently in the pipeline.
- The lack of promising materials to work on is a weakness.
- This is one CoE whose time has not come yet since there are no viable hydrogen storage materials available that meets DOE H_2 storage material targets. The lack of cost considerations is a real weakness.

Specific recommendations and additions or deletions to the work scope

- The reviewer strongly recommends that the Engineering CoE increases the portion of the budget for prototype testing and invite people from the Metal Hydride CoE.
- Safety, codes and standards are critical for system development and acceptance by the society. However, this project does not contain and/or collaborate with those who engaged in these issues. It is strongly recommended that the Engineering CoE communicate, converse with, and collaborate with those people.

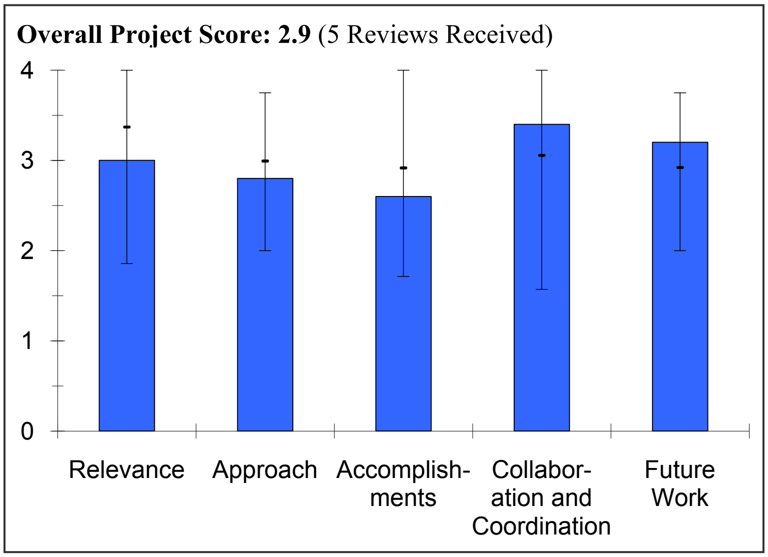
- Doing a risk assessment is also significant for applications and should be included in the objective of the project.
- As the last remaining CoE, this center has the added responsibility to maintain and preserve the institutional memory of the entire hydrogen program. The current level of interaction and the specific leveraging of the other centers is not adequate.
- It remains to be seen whether allocating 15% of resources to the prototype development and/or testing will be adequate. It may very well be enough depending on what criteria are used for the go/no-go points.
- Much of the system design engineering work has been done in parts in various projects and there should be efforts to use this knowledge.
- Since there are some duplicate efforts in subprojects there needs to be some rationalization or centralization of the work beyond what is proposed.
- Some research on hydrogen storage materials has to continue, because after five years of the Material CoEs there still is not a specific hydrogen storage material that meets the DoE's gravimetric and volumetric system targets, and other targets that haven't been demonstrated. Hydrogen storage projects that are going to continue beyond the Material CoEs must be responsive to the needs of the Engineering CoE.
- Given that the Materials CoEs are terminating this year, it is unclear how new materials ideas will be input to the Engineering CoE and how feedback from the Engineering CoE to materials researchers will take place. With the termination of the Materials CoE work, advances in emergent materials properties are unlikely to be forthcoming. It is not apparent that engineering solutions can overcome the shortcomings in inherent material performance. This issue should be addressed more explicitly by the Engineering CoE and the DOE.
- This CoE should consider formally bringing ANL and TIAX into the CoE. Their efforts are integral to what is being done. In any event, the Engineering CoE should not duplicate ANL and TIAX efforts.
- The PIs need to add cost considerations and justify continuation in the absence of viable hydrogen storage materials.

Project # ST-05: Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

Darrell Herling; Pacific Northwest National Laboratory

Brief Summary of Project

The overall technical objectives of this project are to: 1) design a chemical hydride hydrogen storage system and balance plant components, 2) reduce system volume and weight and optimize storage capability, fueling, and hydrogen supply performance, 3) mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability, 4) demonstrate the performance of economical, compact, lightweight vessels for hybridized storage, and 5) guide the design and technology down selection through cost modeling and manufacturing analysis.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- As a key member of the Hydrogen Storage Engineering Center of Excellence (Engineering CoE), Pacific Northwest National Laboratory (PNNL) has a primary responsibility to develop and assess the solid phase ammonia borane (AB) as a viable hydrogen storage system that can meet the 2015 DOE performance targets. PNNL also plays a lead role in the assessment and modeling of selected metal hydrides and structural materials and/or components in support of the general Engineering CoE program. PNNL has proposed initial concepts and have performed its first phase modeling on a solid AB storage system. While this system may satisfy some targets, it looks to be a rather complex configuration by requiring transport of as-prepared fuel and spent AB pellets into and out of a reactor aboard a moving vehicle. This approach is fraught with difficulties in many aspects related to the probable combination of high pressures (up to approximately 500 bar) and temperatures possibly as high as 500 °C combined with the foaming of AB during hydrogen release. Thermal management as well as materials compatibilities look very challenging. At this time, there are reservations that PNNL can devise a practical and robust storage system based upon their current configuration for solid AB pellets.
- This project addresses many (about 10) barriers that are critical to the success of the Hydrogen Storage Program and fully supports DOE RD&D goals and objectives. There are a great many things going on in this project. Hopefully, these many pieces of the project will remain well integrated in the coming years.
- The comment about creating a system for materials with several obvious issues might be a hurdle toward reaching the DOE targets.
- It is uncertain that the end point of the research would lead to a practical storage system with practical system density, system H_2 mass fraction, simplicity, and cost.
- The storage costs are an important element with respect to enabling cost effective, on-board hydrogen storage and hydrogen vehicles.

Question 2: Approach to performing the research and development

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

- PNNL currently appears to have two major roles in the Engineering CoE: 1) Consolidate and assess the properties of chemical storage and/or metal hydride storage media and structural materials such as carbon and steel containers and 2) develop an on-board hydrogen storage system based on solid AB decomposition.

- Both tasks are relevant at this phase of the Engineering CoE. It is unclear whether a truly viable storage system can be achieved based on AB decomposition because of the need for thermal control of this strong of an exothermic reaction and the physical changes that occur in AB as hydrogen is released. The role and approach of PNNL to determine the materials properties of storage media and materials seems sufficiently broadbased and thorough enough to be of value to the DOE storage program, irrespective of the challenges with solid AB storage.
- There are many different types of work going on in this project. Giving the benefit of the doubt to the team performing the various tasks, the approach seems to be appropriate and effective. It is hard to say that there is a particularly sharp focus on any one technical barrier because of all the different studies that are in progress.
- There is an issue focusing on creating a system for neat AB that suffers from impurities forming and several other issues that could be improved by using ionic liquids, for example. It would be worthwhile to consider refocusing the effort on the most promising AB systems, like AB/ionic liquids, rather than neat AB.
- The H_2 ballast tank used for vehicle propulsion during reactor warm-up is an old concept, prior to hybrid electrics and plug-in hybrid electrics. A hybrid car battery may obliviate any benefit of a hydrogen ballast tank for this energy storage need. However, for a load following functionto buffer the reactor, a ballast tank may be relevant.
- Overall, the approach is well structured, but the effort would benefit from inclusion or consultation with people who have developed prototype chemical hydride systems previously, Chrysler and Millennium Cell, in particular.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.6** based on accomplishments.

- In the nominal 16 months since work in the Engineering CoE commenced, PNNL has made good progress in developing and initially assessing an innovative solid AB hydrogen storage system. However, there are various unresolved issues with this concept relating to pellet handling, temperature management, minimizing hydrogen losses during fuel loading and unloading and operating, and the arrangement of the various components, such as storage of pellets, augers, and reactors. These issues need significant resolution prior to the go/no-go review in March 2011. A number of interesting properties on other storage media and structural materials have been collected and, at least initially, evaluated by PNNL. PNNL has not done much yet with other potential chemical storage media, namely liquid AB, alane, Lithium aluminium hydride ($LiAlH_4$), and liquid organic carriers, and these warrant more attention as back-up to the solid AB approach. In any case, there has been a significant amount of positive results at PNNL since the start of the Engineering CoE.
- Significant is the right way to describe the collective progress toward meeting objectives and overcoming one or more barriers. It was overwhelmeding to follow the number of presentation slides, including the supporting slides. Clearly, there is a lot of on-going work for the allocated funding source, possibly too much activity. Trying to tackle 10 barriers with $1.5 million per year may become problematic in the long run.
- The summary of accomplishments is more a list of what was done rather than what was learned.
- There is little indication of technical or cost-target progress mentioned in the main presentation. There is some information in the backup slide,s but it is not clearly presented.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- PNNL appears to be actively participating with its partners in the Engineering CoE as well as other research groups at ANL, TIAX, and the CHCoE. The information interchanges look to have been very productive.
- Slide 31 presents a clear picture of the roles and responsibilities for the partnering in this project. This slide gives a sense that the collaboration and coordination aspects of the project are appropriate and effective.
- More visible collaboration with ANL and TIAX is recommended, since it is not so obvious.
- There is a good list of collaborators, but cross fertilization is not obvious.
- There appears to be a good interchange with other Engineering CoE participants, but the project team should consult with former chemical hydride system developers.

Question 5: Approach to and relevance of proposed future research

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

- PNNL presented a strong plan for their activities in the coming year. They aggressively should prepare for the go/no-go review with respect not only to the solid AB storage options, but also the alternative systems identified on slide 35 for the AMR presentation.
- The future plans are consistent with the goals and objectives of the project. At this point in time, good is an accurate description of the planning because the tone of the planning is still in a very generalized state. As more concrete results are obtained (e.g., for go/no-go decisions), planning targets should sharpen considerably. It would be good to see more achievement statements in the future plans and less "determine this" and "complete that" type plans.
- For all AB and other non-reversible systems, special focus should be given to finding working strategies to recover the spent fuel. However, it does not seem to have the highest priority.
- The technical side of the effort is reasonably laid out, but there needs to be more emphasis on evaluating projected costs.

Strengths and weaknesses

Strengths

- PNNL has built upon its extensive AB development effort from their CHCoE research while directing their current efforts directly towards the critical engineering issues for a solid AB storage system. They have developed a viable thermal modeling effort for the solid AB storage designs. The properties for a number of structural materials have been compiled and evaluated. Good directions for next stage efforts are identified.
- The project team is well organized and ambitious.
- They exhibit strengths in engineering modeling and balance of plant.

Weaknesses

- PNNL has invested much of its manpower and resources on the complicated and risky concept of on-board storage using solid AB pellets that must be transported into a variety of locations, probably at the expense of other options. The issues related to impurities released from decomposing AB phases do not seem to have been seriously considered in their system designs.
- Their project goals are perhaps too ambitious for the allocated funding.
- The selection and focus on creating a system for neat ammonia borane selected suffers from the impurities formation, unless it is placed in scaffolds or ionic liquids. It will be worthwhile to consider the most promising AB systems, like ionic liquids-AB, rather than neat AB.
- For all AB and other non-reversible systems, special focus should be given to finding working strategies to recover the related spent fuel.
- Not assessing the risk in shipping and storing ammonia borane based on its reactivity at temperatures found in some shipping and storage environments is a weakness.
- There needs to be more emphasis on evaluating projected costs.

Specific recommendations and additions or deletions to the work scope

- More effort needs to be devoted to the other chemical storage options as the solid AB system probably will be extremely difficult to achieve for vehicle applications. Rather than devote a lot of energy into the resolution of the solid AB problems, look at requirements and benefits of these alternative approaches. In any case, the go/no-go review should include a very hard check of the feasibility of solid AB storage.
- It's hard to appreciate all the details of a project with such a broad scope in a 20-minute talk. With 36 slides to take in, it’s possible to have missed some of the important messages. Perhaps in 2011, emphasis could be placed on the most informative and compelling results.
- Do keep the project; however, its recommended that it refocuses on more promising AB systems.

- The creation of a real system and just relying on calculations is recommended.
- It is suggested that the PIs initatie more interaction among modeling partners, OEMs and engineering CoEs to accelerate model-based development.
- Do a critical, comparative assessment between the hydrogen ballast tank and hybrid vehicle battery for propulsion during reactor warm-up.
- Make a preliminary cost assessment as a high priority since having a technology that is technically feasible is insufficient.

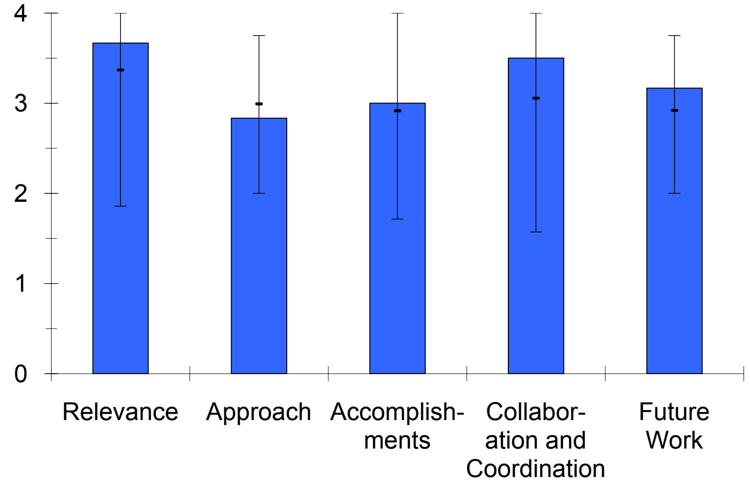
Project # ST-06: Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

Dan Mosher; United Technologies' Research Center

Brief Summary of Project

The objective of this project is to design materials-based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles. The project focuses on metal hydride, chemical hydride, and hydrogen cryo-sorption materials for hydrogen storage.

Overall Project Score: 3.2 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.7** for its relevance to DOE objectives.

- The project team presents a good understanding of materials compaction and stabilization, which is critical to designing automotive storage systems.
- This project addresses the DOE targets.
- This project fully supports the Hydrogen Storage Program by directly addressing key DOE RD&D goals and objectives. Specifically, it is focused on the design of materials-based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles. How much more relevant could a Engineering CoE project be?
- For the transition of materials technology from the laboratory to real-world, working storage system prototypes are an extremely important aspect of the hydrogen program. However, there are clearly a number of vacancies in critical materials data that will need to be addressed, or should have already been addressed by the Materials CoEs. For example, the affects of material compaction on the intrinsic gravimetric and volumetric capacity was brought to the forefront three or four years ago, yet no comprehensive study was ever initiated among the CoEs to address this important property. The burden is now on the Engineering CoE to fill in the gaps without a cohesive organization of the Materials CoE.
- By its integration into the Engineering CoE, this project covers key components addressing the quantitative DOE storage targets and barriers.

Question 2: Approach to performing the research and development

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

- As with most of the Engineering CoE principal investigators (PIs), they have many seemingly unrelated tasks. The most important is likely the materials compaction and stabilization in the systems. This is the reason all the projects in the Engineering CoE will lose at least one point for approach.
- Their approach to design proper systems seems to be very good.
- The approach is fairly standard, and the United Technologies Research Center (UTRC) team has done system design work in a previous DOE-funded program. It is not clear what has been learned or leveraged from the previous system design and what is carried over to this program.
- There is a higher expectation from a team and/ or organization that has been involved in the same specific work and funded by the same funding agency. No new innovative engineering solutions were presented.
- This project is indeed sharply focused on critical technical barriers. Simply stated, the approach involves leveraging of in-house expertise and experience in various engineering disciplines with metal hydride system prototyping to advance materials-based hydrogen storage for 300-mile range automotive applications.

- To those on the outside, there appears to be a significant amount of repetition planned in the approach relative to experimental measurements of intrinsic material properties. While this actually may not be true, it is recommended that a matrix of missing properties be prepared so that the Engineering CoE can justify the experimental efforts and delineate this from data that may or may not already be available within the Materials CoE.
- The approach is reasonable; UTRC uses its past expertise and experience to contribute to several specific areas within the Engineering CoE, as mentioned on slide 4. It leads the efforts on reactivity and compatibility, H_2 purity, forecourt requirements, and risk assessment and mitigation on slide 5.
- There are many areas of effort listed. It is not clear that all can or will be done, and whether possible areas of duplication will be avoided.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- This project receives a good rating.
- To take sodium alanate ($NaAlH_4$) as the test material is very good idea, even if $NaAlH_4$ itself does not meet the DOE target.
- Well-defined material for fundamental studies is needed.
- The project is still in its early stages.
- There is impressive progress in several key areas:
- The project shows good progress in the area of improved volumetric capacity and thermal conductivity through compaction.
- They showed that $NaAlH_4$ is a good model material but cannot achieve gravimetric capacity targets at fast refueling times.
- The project team showed that a hydrogen purification cartridge for adsorbing ammonia (NH_3) appears viable.
- They established a framework for performance comparisons of all three hydrogen storage materials against DOE targets on a common basis.
- Good progress is shown in light of the early stage of the program.
- Although this project is relatively new, it seems like some good progress has been made so far.
- Hydride compaction has impressively increased density and thermal conductivity.
- The reactor modeling suggests that it will be difficult to reach the DOE combination of gravimetric capacity and refueling time. Although this is a negative result, it is important to know.
- H_2 impurity work in this project suggests that a disposable purifier is the best approach to remove deleterious impurities such as NH_3 from H_2 exiting ammonia borane and amide storage media. It is implied that the purity target can be met at less than one part per million of NH_3.
- The PIs'vehicle simulation modeling seems to be making good headway.
- There are other areas within UTRC's responsibilities that are not mentioned that are under progress, namely reactivity and compatibility. It is unclear whether work in these areas has started.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.5** for technology transfer and collaboration.

- The PIs are working with all the appropriate Engineering CoE researchers and OEMs.
- UTRC collaborates with a wide range of contributors of this project.
- Collaborations with other institutions and partners are well coordinated. Ford Motor Company, General Motors, Pacific Northwest National Laboratory and the National Renewable Energy Laboratory are working together on system-level modeling. The collaborations must be working well, because the progress-per-project-dollar has been excellent.
- On paper, the collaboration structure of the Engineering CoE seems excellent.
- It is not clear how strong the collaboration is. There are possible small overlaps. Has duplication been avoided so far?

Question 5: Approach to and relevance of proposed future research

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

- There are a lot of tasks so it might be beneficial if they concentrate on a few of them at a time. This is symptomatic of all the partners in the Engineering CoE.
- Impurity getters may be a necessary evil at this point. As much as possible, the DOE should favor impurity prevention over filtering projects since filtering could imply the loss of backbone material like cycling capacity.
- Their work should focus on the materials compaction studies and stabilization efforts, namely aluminum mesh. These techniques and designs are the critical missing information links between the systems and materials developers.
- The future plan sounds good.
- It is unclear how much of the proposed work is actually had been completed or being replicated from the previously funded project.
- Because of the history of the previous system design work of the UTRC within the DOE hydrogen program, the PIs of this project must clarify the proposed work from the previously performed work. There is considerable duplicating of tasks within the project.
- Slide 15 of the presentation is a perfect future plan portrayal. It lists the objectives that are all well framed and appropriate and gives milestones for completion. This same slide should appear in the 2011 presentation with indications of how the project has progressed.
- They must assess a matrix of missing properties before moving forward.
- This project seems fully appropriate and within the needs and objectives of the Engineering CoE.

Strengths and weaknesses

Strengths

- The design of the system and the R&D of technologies needed for the system are the strong points of this project.
- The project team is well organized, properly focused, and productive.
- They exhibit the much needed effort to accelerate the transition of storage materials technology to useful, fully characterized storage systems.
- The project has the potential to identify critical data, such as intrinsic material properties, that may be missing, and have that data quickly generated among the four CoEs.
- This project team includes good engineering capability and experience.
- UTRC's past work modeling, building, and testing prototype hydride containers are great pluses.

Weaknesses

- Safety, codes and standards are not included in the presentation or even as a subject for collaboration.
- None discerned.
- There appears to be a large potential for redundancies in both experimental measurements and system modeling. This perception, whether real or not, needs to be addressed.
- There was no clear pathway defined on how candidate materials emerging from the Materials CoEs will be selected, and who within the overall organization will make that decision.
- There seems to be a possible overlap with Los Alamos National Laboratory (LANL) on purification beds for H_2 from ammonia borane. Hopefully, there is complete collaboration there. The PI said there are direct interactions with LANL on this.

Specific recommendations and additions or deletions to the work scope

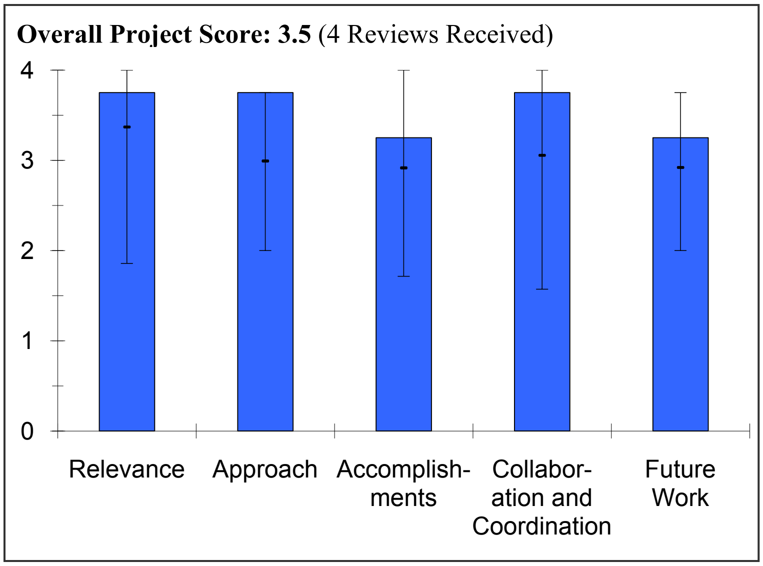
- This project should collaborate with people on the safety, codes and standards. Without these issues addressed, the system may not stand and be robust.
- Because of the history of the previous system design work at UTRC in the DOE hydrogen program, the PIs of this project must delineate the proposed work from the previously performed work. There is considerable duplicating of tasks within the project.

- It is understandable to have access to UTRC expertise and project institutional memory. As a result, the performance and expectations from this project are higher than other projects.
- The presentation was excellently planned out in terms of having the right number of slides as opposed to having way too many, as most presenters did. And, the slides presented a clear picture of what was accomplished, how it was done, and what it meant in terms of goals and objectives.
- A matrix of missing properties should be prepared so that the Engineering CoE can justify the experimental efforts and delineate this from data that may (or may not) already be available within the Materials CoE.
- The UTRC disposable purifier should be tested with a proton exchange membrane fuel cell as per the LANL approach to firmly establish its viability. During Q&A session it was stated such FC tests are planned.

Project # ST-07: Chemical Hydride Rate Modeling, Validation, and System Demonstration

Troy Semelsberger; Los Alamos National Laboratory

Brief Summary of Project



In support of the goals and objectives of the Hydrogen Storage Engineering Center of Excellence (Engineering CoE), Los Alamos National Laboratory (LANL) will contribute to modeling, designing, fabricating, and testing a prototype hydrogen release reactor for a hydrogen storage system based on chemical hydrides. Objectives for the project are to: 1) develop fuel gauge sensors for hydrogen storage media, 2) develop models of the aging characteristics of hydrogen storage materials, 3) develop rate expressions of hydrogen release for chemical hydrides, 4) develop novel reactor designs for start-up and transient operation for chemical hydrides, 5) identify hydrogen impurities and develop novel impurity mitigation strategies, and 6) design, build, and demonstrate a subscale prototype reactor using liquid or slurry phase chemical hydrides.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.8** for its relevance to DOE objectives.

- This project is highly relavent. Accurate fuel level monitoring of H_2 in solid state materials has been difficult and cumbersome to measure. A simple, cost-effective, and tunable system is required.
- Materials aging characteristics are important
- To investigate a system using a small-scale prototype strongly supports the Hydrogen Storage Program. Engineering success is indispensable in realizing the hydrogen economy.
- This project addresses critical issues in the implementation of chemical hydrides in a hydrogen storage system and also seeks to develop key enabling technologies for other hydrogen storage system types. The tasks of this project must be accomplished to assure that system parameters are well defined, and key enabling technologies are sufficiently well developed such that reliable systems analysis and prototype testing can be accomplished for chemical hydride-based fuel cells.
- The project addresses some areas that are critical to DOE's hydrogen program. Specifically, they are the development of fuel gauge sensors, models of aging of hydrogen storage materials, novel reactor designs, and building a subscale prototype reactor.

Question 2: Approach to performing the research and development

This project was rated **3.8** on its approach.

- The principal investigator’s (PI) approach is good but it is suggested they concentrate on two topics as opposed to four, specifically in order of priority, the fuel gauge and tank integrity work are the key topics on which they should focus.
- This project contains various and significantly important pieces of technologies for the engineering of hydrogen storage materials.
- If not outstanding, this project is certainly very good and is rated at 3 or higher. The project is indeed well designed and well integrated with other closely related efforts. Each of the seven tasks focuses on a critical issue. It is doubtful, however, that all the critical issues for chemical hydride-based systems are covered, but the

ones that are covered do need to be addressed. Some of the approaches to specific critical issues are highly innovative and show a keen sensitivity to what it will take to meet performance targets for 2015 and beyond.
- The project focuses on significant technical barriers.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.3** based on accomplishments.

- This project is excellent, particularly on the fuel gauge work. No PI has worked on this issue before. It is an often overlooked but a critically important requirement for constructing automotive systems. The task is not trivial.
- It is a great success to develop a homemade acoustic hydrogen fuel sensor. The shelf-life modeling study is a little bit behind the schedule but others are on or ahead of schedule.
- The project is off to a good start. Closure on some of the tasks is in sight. There is clear evidence that the project is driven by a full understanding and appreciation of DOE goals and targets. Even at what is considered to be a lean funding level, good progress is being made on a majority of the seven tasks.
- Acoustic sensors appear to be an interesting solution. Proof of concept is demonstrated.
- Current models for shelf life of ammonia borane (AB) were found to be inadequate.
- Reaction models for hydrogen release need to be refined.
- Low-temperature dehydrogenation catalysts for AB have not been found to date.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.8** for technology transfer and collaboration.

- The project team is working with the appropriate partners in the Engineering CoE .
- LANL leads the team and seems to be well organized.
- The project appears to be exceptionally well coordinated. Partnering looks to be appropriate and seemingly well linked to the individual tasks. The Material CoEs have consistently demonstrated acute attention to well-coordinated, effective, collegial collaboration, and it appears the Engineering CoE will follow that path as well.
- Collaborations among the CoEs are excellent.

Question 5: Approach to and relevance of proposed future research

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

- It is strongly recommended to include the fuel gauge work into future tank builds in the Engineering CoE.
- This reviewer questions whether a 100-g tank that the center plans to build be able to accommodate the project’s objectives, including whether materials aging predictions be validated in small 100-g tanks?
- It is recommended that the PIs deemphasize impurity getters in favor of projects that mitigate impurities by preventing the breakdown of the storage material such as diborane and borazine, among others.
- The future work proposed is appropriate, however, the size of the prototype seems to be small.
- Proposed future work is planned in a logical manner with appropriate decision points. The barriers to progress are understood. The need to consider alternate development pathways is recognized by the PI.

Strengths and weaknesses

Strengths

- This project contains the technologies that are necessary to fabricate a hydrogen storage tank using hydrogen storage materials from a fuel-sensing system to the tank.
- This team’s PI is knowledgeable, enthusiastic and fully dedicated. His poster presentation was excellent. That presentation demonstrated the kind of commitment to success that is needed for the goals of this project to be reached.
- The project team comprises a group of participating partners that are veterans in the hydrogen storage and fuel cell community.

- The project addresses a number of important issues. If it's successful, the system design will be more refined.

Weaknesses

- It seems to be a little bit uncertain that the design concept of the tank is using AB as the hydrogen media.
- At a funding level of a little more than $700,000 in fiscal year FY 10 and no clear information about what the funding will be in future years, it will be difficult to plan and manage this technically diverse project and to achieve the goals in a timely manner. With seven tasks in all, the FY 10 budget breaks down to about $100,000 per task. That doesn't buy much effort at national laboratories in this day and age.
- None.

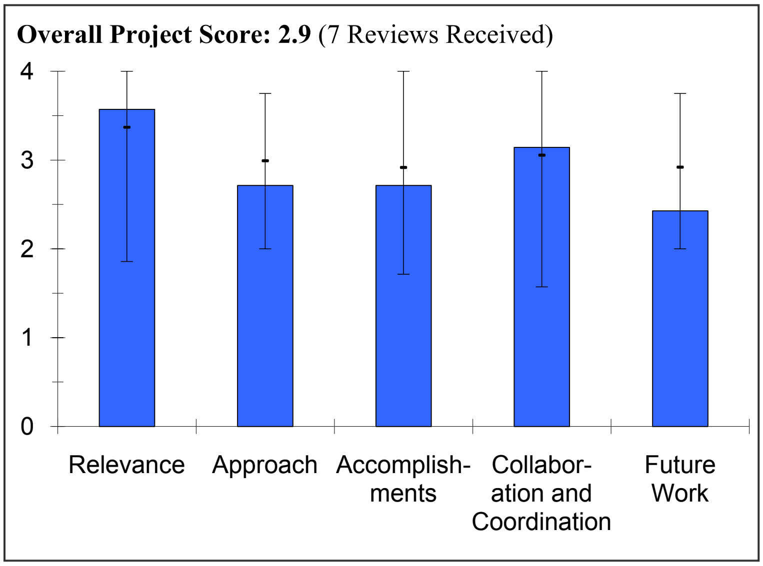
Specific recommendations and additions or deletions to the work scope

- The size of the prototype should be larger. In case of ammonia borane, regeneration of AB on a larger scale may be tested in the proper scale.
- At the present funding level, the scope may already be too broad.
- The slide presentation for this project was very comprehensive and informative. One aspect that could use more emphasis in future years is to show where each partner organization fits into specific tasks and to give an indication of their role in the task somewhere in the task description.
- None.

Project # ST-08: System Design, Analysis, Modeling, and Media Engineering Properties for Hydrogen Energy Storage

Matthew Thornton; National Renewable Energy Laboratory

Brief Summary of Project



The overall objective for this National Renewable Energy Laboratory (NREL) project is to provide system design, analysis, modeling, and media engineering properties for hydrogen energy storage. Objectives for the project are to: 1) manage Hydrogen Storage Engineering Center of Excellence (Engineering CoE) performance, cost, and energy analysis technology area, 2) develop and apply a model for evaluating hydrogen storage requirements, performance, and cost trade-offs at the vehicle system level, 3) perform hydrogen storage system well-to-wheels (WTW) energy analysis to evaluate greenhouse gas (GHG) impacts with a focus on storage system parameters, vehicle performance, and refueling interface sensitivities, and 4) assist the Engineering CoE in the identification and characterization of sorbent materials that have the potential for meeting DOE technical targets as an on-board system.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- The relevance of this project is generally high. Systems-level knowledge is required to understand how to build an automotive-grade tank
- This project meets the target of the Hydrogen Storage Program at present. However, that is uncertain in the near future.
- This project aims to address some of the key barriers to hydrogen storage. The modeling is an extremely useful tool to identify how various hydrogen storage systems might behave in a fuel cell (FC) vehicle.
- This project is a key piece of the Engineering CoE. The emphasis is on performance, cost, and energy analysis, modeling and evaluation of hydrogen storage requirements at the vehicle level, WTW energy analysis and GHG impacts assessment, and identification and characterization of sorbent materials that have the potential to meet DOE technical targets for on-board systems. All of these focal points are critical to meeting DOE RD&D objectives.
- It is not entirely clear the extent to which design, analysis, and modeling will cover vehicle systems. A diagram or table of vehicle system components would have been useful here.
- High-level integration of storage characteristics into vehicular performance requirements, such as performance and emissions, is an important effort to help coordinate and integrate several different areas and to gauge subsystems' effectiveness. This type of effort is also very useful in establishing or modifying technical targets.
- This effort is part of the Engineering CoE, which is clearly oriented toward the DOE's targets and technical barriers.

Question 2: Approach to performing the research and development

This project was rated **2.7** on its approach.

- A clear explanation of the viability index was not provided. These kinds of statements are dangerous to make without OEM involvement and are likely to be considered proprietary as well. If it is based on only two vehicle types from 2004 data, this hardly seems like a representative vehicle set.
- The PI did not explain what design envelope was considered for allowing powertrain component sizing to float. For example, it was not clear whether the PI is using DOE targets for other FreedomCAR technical teams for fuel cells, power electronics, and vehicle weight. Similarly, it is not clear whether the model assumes all targets will be met or partially met or whether the model is based on current vehicle component sizing. No information was provided for vehicle-type and performance baselines.
- The WTW analyses seem outside the intended scope, are potentially mission creep, and are redundant to efforts with H2A models already in existence.
- It is not clear what vehicle modeling is. If they really wish to do so, representation from the car industry should be invited.
- The term "viability index" was used for sensitivity analysis. However, the definition of a viability index has not been shown clearly. It is a question that trades off between cost and vehicle performance and which is critical. Are these two factors really in trade-off relations and is that significantly important?
- The approach to meeting the project objectives makes sense if the investigators can get the data they need to run their models.
- It would be useful to show a plot comparing the performance of the various H_2 fuel cell systems against the performance of an electric vehicle or hybrid electric vehicle. Obviously, this could only be done later in the project, once the vehicle and FC storage models are integrated. But, this will give us a much better sense of how far away they are from a viable system.
- Not much has been done yet. At the present stage of the project, the approach is rather loosely developed. Presumably, more details about the approach will be available for presentation next year.
- No clear approach was presented.
- All tasks are well conceived toward executing the work and are well integrated with other efforts. Go/no-go decision points seem to be related to what is being assessed rather than this specific effort.
- This project serves to manage and participate in the general area of vehicle performance, cost, and energy analysis. This is an important effort within the Engineering CoE and interacts with several other CoE participants, including the OEMs GM and Ford.
- NREL is developing the important model that connects the vehicle performance and cost with the storage media parameters.
- There are several other Engineering CoE partners helping with the modeling effort. It is not clear how the others contribute to this approach.
- The project team's WTW analysis is important.
- It is highly logical that NREL is so active in adsorption media property development within NREL and among other members of the Hydrogen Sorption CoE.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- The project is showing good progress so far.
- The model shown here does not seem to fit the request from the car industry.
- The definition of viability index is not clearly explained.
- Preliminary results on GHG emission and WTW efficiency figures need to be improved very much and seems to be very much behind schedule.
- The project's accomplishments seem a little weak. The investigators claim they have validated models, but where are the data? They have link/run models/simulations listed under milestones for July 2009 but haven't really shown any data. The key plot that seems to be missing is a comparison of the modeling results with some real experimental data to demonstrate that the model gives reliable results.
- The project is not far enough along to gauge its success in terms of meeting objectives and demonstrating targets. Slides 7-10 don't present much of a message, other than to create the impression that the project's computational tools address the issues at a high level of detail. The viability index study stands out as a seminal, path-directing finding, but not one that is at all surprising. WTW and GHG results are just preliminary.

- There is good progress on the development of a hydrogen storage vehicle model. However, it was unclear how much of the total vehicle this modeling platform takes into consideration. For example, it is not clear whether the modeling considers drivetrain components and vehicle dynamics.
- The so-called viability index needs a clearer definition. Examples should be given to aid in the interpretation of this metric.
- The principal factors contributing to the WTW and GHG comparisons need to be defined.
- Technical accomplishments to date are acceptable and appropriate for the project schedule.
- A rather large number of accomplishments were cited.
- The Hydrogen Storage Simulation (HSSIM) model has been developed. Examples of the needed inputs and outputs were shown, but the general working mode was not disclosed in any detail. A few preliminary results were cited. Apparently, much progress is expected in the next year.
- WTW and GHG analyses have not really started, yet the preliminaries are underway. Work with thStorage Systems Analysis Working Group (SSAWG) and Greenhouse gases, Regulated Emissions and Energy in use Transportation (GREET) model has just begun, but the details of those connections were not made very clear.
- The team's progress has been especially good in understanding the potential of sorption media.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- The project team is working with the appropriate Engineering CoE and OEM partners.
- Collaboration is a little bit poor.
- The investigators seem to be collaborating well with other Engineering CoE partners. Key questions are: Where are the investigators going to get the materials data on the new materials needed to run the models? Are there any collaborations with materials groups that can supply the necessary input parameters?
- There are numerous, seemingly appropriate partners and collaborators, but the specifics of the roles and responsibilities of the individual partners were not clearly spelled out in this presentation.
- The project is well coordinated with a number of other organizations and efforts.
- Connections to the partners in the Engineering CoE, as well as the other DOE CoEs are listed in slide 2, but there is very little detail on exactly how those collaborations work. Without that detail, it is difficult to determine the true level and practical function of such collaborations.
- There is interest in the knowing more about the communication mechanisms with the partners and how successful those communications have been for the NREL modeling activities, such as the input from the OEMs GM and Ford. The Engineering CoE's general presentation and the Ford presentation did fill in some of the gaps.

Question 5: Approach to and relevance of proposed future research

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

- The PI should deemphasize WTW work and concentrate on modeling the storage system requirements such as buffer capacity requirements, heat flux of coolants, and fuels.
- The PI needs to show a systems sensitivity chart based on the likelihood of meeting FreedomCAR technical team targets.
- The presentation needs to show vehicle type and performance baselines that the model is based on.
- The material requirements from the engineering point of view may not be accepted by material scientists and should be in the sense of materials.
- This project is a modeling study but not a study of material development. The first description in the viewgraph of the future work cannot be understood.
- The first line under the future work section states that to meet DOE 2015 targets, new materials must be used, but it is not clear where these materials are coming from. The problem with the future work plan is really a problem with the entire Engineering CoE, not just this project. The Engineering CoE was established on a feedback principle where the input parameters for this type of modeling were coming from the materials CoEs. Now that the materials CoEs are gone, it is not clear where the Engineering CoE will get the materials properties to run the models. It seems that this project and the Engineering CoE are stuck with existing data in

the literature. It may not make sense to continue looking at a sodium alanate tank when it's already known it will never meet DOE targets.
- It's as good as possible at this time. Hopefully, in the coming year as progress is made in the various task areas, the more general nature of the plans presented at the review will sharpen. The viability index plots and spider web charts should serve as meaningful portrayals of progress.
- There is not enough information presented to clearly understand what's missing in the various modules of the vehicle model and what features exactly will be integrated in future versions. The future work for new sorbent materials, which includes the measurement of intrinsic storage capacities, kinetics, and so forth, seems redundant since most of this has already been completed.
- This is good. The future tasks are clearly identified, though some additional information regarding how they are interrelated and scheduled would be helpful. The media engineering task's future work needs more clarity relative to schedule and decision points.
- The future work plans seem reasonable. Special effort must be put forth to avoid duplication with other DOE-supported modeling activities. The possibility for good synergy is there.

Strengths and weaknesses

Strengths
- This project carries out modeling to vehicle performance from material properties.
- WTW efficiency and GHG emissions will be analyzed.
- Computer modeling will be very useful to evaluate different tank designs, especially once the model is integrated with the FC models.
- This project's staff is well qualified, informed, and dedicated.
- The project is starting from a position of strength in terms of defining and addressing the issues based on the progress made in recent years by the material CoEs and within other parts of the Fuel Cell Technologies Program.
- If total vehicle performance modeling is the goal here, then the project has the potential to quickly evaluate storage system characteristics and how they impact total vehicle mobility.
- The project team presented a good, overarching program to integrate and assess a number of other more detailed efforts.
- Their team comprises members with past experience with modeling and vehicular systems.
- They have a close connection to NREL and Hydrogen Sorption CoE sorption activities.

Weaknesses
- The materials to be analyzed are limited to sorbents, and a proper sorbent for real application does not exist. It cannot be understood that modeling to optimize the system is carried out independently for each material such as chemical hydrides, metal hydrides and sorbents.
- The accomplishments seemed a little weak. In the future, more data should be presented.
- The PIs should also present a clear plan for how they are going to evaluate new materials in the absence of the materials CoEs.
- No significant weaknesses here.
- It is suggested that, in future years, slides like 7-10 be replaced with simple graphics that give the big picture of what the modeling and evaluation studies are showing. It's certain that the codes work properly and produce a plethora of numbers. The bottom lines are what the reviewers want to hear and see.
- A clear description of the big picture relative to the vehicle modeling is lacking. This deficiency can be corrected by showing a diagram or table that lists the pervasiveness of the vehicle model and exactly what systems will be taken into consideration.
- A clear approach toward the project objectives was not described.
- The future work for new sorbent materials, which includes measurement of intrinsic storage capacities, kinetics, among others, seems redundant since most of this has already been completed. The project team needs to assess what data is actually missing before moving forward with additional analyses.
- The project's collaborations are not clearly established. They are very important for this project.

Specific recommendations and additions or deletions to the work scope

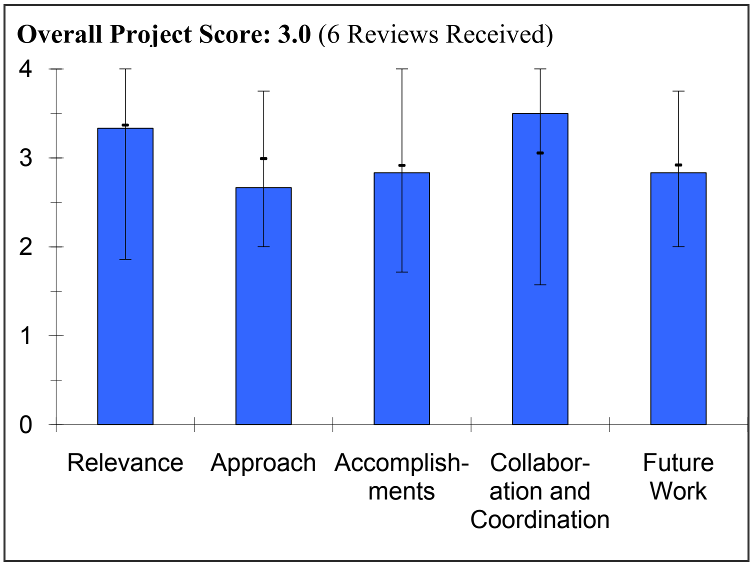
- This project tries to treat a wide range of issues, but it should be focused to a few significantly important ones.
- It seems that the Engineering CoE needs to be completely reorganized given the loss of the materials CoEs. It may be worth including some materials development work in the Engineering CoE.
- The Media Engineering Properties task requires that some efforts continue within the Fuel Cell Technologies office to develop hydrogen storage materials. The materials needed to meet all the targets on the boundary of the spider web are still not in hand.
- In future briefings, a diagram of what vehicle systems are included in the vehicle modeling would be extremely helpful.
- The project team should develop an approach detailing how each of the major goals of the project will be accomplished.
- The PI needs to assess what material property data is missing before proceeding with additional measurements.
- None at this time.

Project # ST-09: System Design and Media Structuring for On-Board Hydrogen Storage Technologies

Darsh Kumar; General Motors Company

Brief Summary of Project

The overall objective for this project is to develop systems for on-board storage of hydrogen for motor vehicles. Objectives for the project are to: 1) develop criteria for storage materials in the metal hydride and adsorbent material categories and identify storage materials in those two categories, 2) build system simulation models for metal hydrides, 3) build system simulation models for adsorbent material hydrogen storage systems, 4) explore pelletization of AX-21 and sodium alanate, and 5) work with the National Renewable Energy Laboratory (NREL), the Ford Motor Company, and United Technologies Research Center (UTRC) for integration of hydrogen storage models in a common framework with vehicle system models and fuel cell models.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Sodium alanate as a model material to develop the engineering tools is probably a good candidate for a metal hydride system. However, by using this material, there is a risk of the project experiencing “tunnel vision”.
- This is a new project in the Hydrogen Storage Engineering Center of Excellence (Engineering CoE) and is only 20% complete. However, the objectives appear to be consistent with the overall goals of the Engineering CoE and are relevant. It is too early in the project to judge whether it will contribute substantially to the success of the Engineering CoE.
- This project is critical to accelerating the development of prototype storage systems that accommodate the special needs of candidate storage media.
- This project is providing guidance to the Engineering CoE regarding characteristics of metal hydride and adsorbent systems required for service on board a vehicle. It is very relevant to the DOE program objectives to develop a materials-based hydrogen storage system for transportation applications.
- This project has a logical approach to potentially increasing the practicality of hydrides and adsorbents.
- Storage costs are an important element with respect to enabling cost-effective on-board hydrogen storage and hydrogen vehicles.

Question 2: Approach to performing the research and development

This project was rated **2.7** on its approach.

- The approach to design issues is standard.
- The approach proposed for this project appears to fit well in the overall scheme of the Engineering CoE with a focus on the metal hydride and adsorbent systems. Although the approach is fairly diverse involving both system modeling and pelletization of the storage media, there are questions regarding the system designs, which were the result of a joint Engineering CoE effort. This project team has to work with the design adopted by all of the Engineering CoE partners.
- After five or so years of materials R&D from the Materials CoE, it is surprising that the only materials selected under the current plan of this project are ones that are very conventional. Greater flexibility in the selection of

materials for system design and media structuring is warranted. However, studies on binder effects to improve volumetric capacity are important.
- The approach is sound. The PI identified materials properties for AX-21 and sodium alanate. Neither of these materials is of much interest for automotive applications, but they are being used as placeholders for advanced materials that may be developed, because their properties are considered representative of their class(es) and their properties are available. System simulation models will be developed for each material, then the materials will be pelletized. Finally, the model of the storage system will be integrated with the fuel cell and vehicle system models.
- The approach would be improved if a viable material(s) were identified and its properties were known and used in the analysis and simulation.
- The work plan needs to better describe the timing and phasing of the tasks. Also, the modeling work does not incorporate any model validation steps.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- The PIs have worked on an alanate system under different capacities and programs. There is also ample data in open literature and within the DOE hydrogen program. There is enough data to make a comparative analysis. It would have been useful to have a comparative analysis within the presentation.
- Progress and accomplishments are minimal to date, but it is very early in the effort and perhaps the progress is acceptable. The first task was completed, but they only had an advisory role in this task. Preliminary work on pelletization is good.
- Their accomplishments appear to be consistent with stated objectives and the proposed timeline.
- The accomplishments are reasonable and consistent with the funding level and the amount of time since the project's inception. Various heating schemes were simulated to release hydrogen. A constant rate was found to be most effective of the AX-21 system. A heating rate that followed the load demand for hydrogen was found to be too complex. Both of these systems fall short of the DOE targets. This points out the need for more advanced materials.
- GM indicated the simulation models were partly validated with data from previous work.
- Compacted materials have not been used in the models. There needs to be an account of compaction characteristics and thermal expansion of the materials.
- An estimate of the maximum storage capacity of the system would be helpful to assess the potential for these systems.
- The PI shows good results in the AX-12 pelletization and with use of sodium alanate.
- The project is only showing modest progress towards overcoming barriers, and there is no indication of progress toward cost targets.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.5** for technology transfer and collaboration.

- There are many partners in the Engineering CoE, and they all appear to be working well together. GM appears to be a contributing member to the CoE.
- There seems to be some redundancy among the collaborators. The specific contributions need to be more clearly defined.
- Collaborations are strong among the members of the Engineering CoE. Automotive partners are providing guidance to the researchers regarding the applicability of approaches to the automotive market.
- There is a very good match between the analytical and the practical across the different sub-tasks.
- The partners appear to be reasonably well involved and contributing.

Question 5: Approach to and relevance of proposed future research

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

- Plans for the future appear to be reasonable, sound and consistent with the overall Engineering CoE plans.
- The PI needs to develop a matrix of material candidates that defines how many different types of materials will be evaluated and on what basis the candidates will be selected.
- There was no discussion in the presentation regarding the criteria that must be met for continuation of the project into subsequent phases.
- It is not clear whether the remaining work will take three years to complete. A greater explanation is needed to support the schedule.
- Regarding cryo-adsorbents, it may be useful to compare the system weights and volumes to those of a pressurized cryogenic gas phase H_2 tank. The only key difference between the two is the extra mass of pressure vessel overwrap, which should be less than the mass of the adsorbent.
- The technical side of the effort is reasonably laid out, but there is still no indication of when system costs will be evaluated.

Strengths and weaknesses

Strengths

- The project staff comprises a strong technical team.
- There are strong partnerships with meaningful interactions.
- The project team has an extensive background in experience and expertise with hydrogen storage systems.
- GM certainly has automotive experience and can contribute strongly to system design and integration.
- The project properly addresses key factors in designing and modeling a hydrogen storage system, including the practical requirements for the densification of storage media.
- The integration of the storage system model with vehicle and FC models is being approached as a team effort, drawing from the expertise of several groups.
- The automotive OEMs provide guidance to the Engineering CoE.
- The collaboration and approach both seem to be well adjusted to the project's objectives.

Weaknesses

- No weaknesses are apparent yet, because the project is too new!
- There is a need for greater flexibility in the selection of materials for system design and media structuring. The current selection of materials is narrow and quite conventional.
- From the information presented, there appears to be some redundancy in at least two tasks. For example, three different organizations are assigned to address media compaction.
- From the sodium alanate simulation plots on page 6, the parasitic load from the burner is 22% to 25%, which should significantly derate the useful hydrogen density of the system and proportionally increase vehicle fueling cost.
- Only modest technical progress has been made, and no cost evaluation was offered.

Specific recommendations and additions or deletions to the work scope

- It is not clear if this work is in support of what the transport subgroup is doing within the Engineering CoE, or if there are some duplications.
- The models need to be validated as they are developed.
- Parasitic losses and heat input requirements need to be minimized.
- New storage materials with better hydrogen storage capacity need to be evaluated as they become available, if they do!
- Identifying a go/no-go decision point on the pelletization work would be advisable.
- The project team should prepare a matrix that indicates the number and type of candidate materials to be evaluated.
- The PI should assess the overall scope of the project and remove any potential redundancies from tasks involving multiple organizations.
- It is recommended that the simulation model be compared with the engineering models developed by Argonne National Laboratory for similar systems.

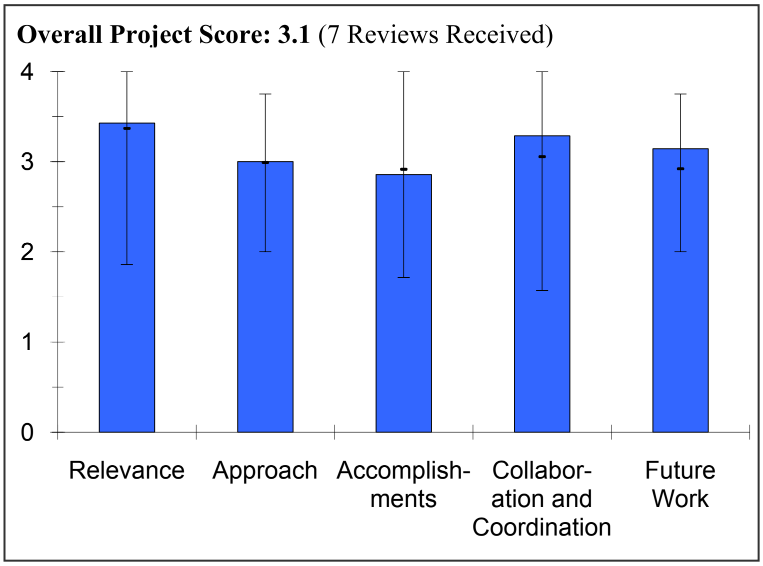
- The simulation models could be used to indicate what material properties would be required to enable the viability of an automotive system.
- The team should make a preliminary cost assessment a high priority since having a technology that is technically feasible is insufficient.

Project # ST-10: Ford/BASF-SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

Andrea Sudik; Ford Motor Company

Brief Summary of Project

This project will address key technical obstacles associated with development of viable hydrogen storage systems for automobile applications. Project goals are to: 1) develop dynamic vehicle parameter model elements for the hydrogen storage system interfaces during realistic operating conditions, 2) develop a manufacturing cost model for hydrogen fuel systems based on a supply chain assessment, and 3) devise and assess optimized, system-focused strategies for packing and processing of framework-based hydrogen storage media.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- This project is addressing a critical issue in the storage system design using reversible carbon-based sorbents.
- This project is very new and only 20% complete. However, the project's role in the Hydrogen Storage Engineering CoE (Engineering CoE) with a focus on metal-organic framework (MOF) storage materials is definitely relevant to the Engineering CoE's objectives and DOE goals and objectives.
- This project focuses on three topics that are critical to developing commercially-viable hydrogen storage systems: system modeling, cost modeling, and materials engineering. Most project aspects are aligned with the Hydrogen Storage Program and DOE RD&D goals and objectives. The project contributes to the system-level assessment and feasibility of framework materials (FM) to meet hydrogen storage targets. To fully appreciate this project, the project team must also have some conviction that the type of FMs chosen for study have a reasonable chance of meeting the entire range of 2015 hydrogen system performance targets.
- The relationship between the Engineering CoE technical goals and the specific project goals are clearly illustrated.
- This project directly supports the objectives of the Engineering CoE. It provided vital OEM support and guidance for the CoE.
- If MOFs are going to play a role in hydrogen storage, this project will be important in optimizing the properties of the material put in the storage vessel and help in understanding dynamics of the vehicle’s propulsion and its hydrogen storage system.
- The storage costs are an important element with respect to enabling cost-effective, on-board hydrogen storage and hydrogen vehicles.

Question 2: Approach to performing the research and development

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

- The PIs are well aware of the solid packing issue of the sorbents. The heat transfer, albeit small, could have a large impact especially in cryogenic or near-cryogenic system.
- The Ford effort focuses on system and cost modeling and identifying approaches for processing MOF-based storage media. The proposed approach appears to be responsive to the task that has been assigned by the Engineering CoE.

- The PIs' project goals and objectives are clearly spelled out and seem appropriate for the type of storage materials chosen for this study. The results of this project should contribute to overcoming some, but not all, barriers to framework material implementation in fuel cell (FC) vehicles. The entire spectrum of subprojects in the Engineering CoE is replete with modeling of one kind or another. Hopefully, at some level, all the modeling efforts will connect in a complementary manner.
- Operating requirements for MOF materials will likely require feedback and/or optimization at the level of material synthesis rather than material processing and/or compaction alone. For example, crystallite size is best optimized during synthesis that may then lead to optimized compaction.
- The modeling effort seems to be duplicated elsewhere with the Engineering CoE. A clearer understanding of how this project's effort differs from similar activities within the CoE is needed.
- The approach is good and addresses several needs within the Engineering CoE. The project provides chemical and physical properties for framework materials such as MOFs. The project also will improve on FC power plant models to account for the dynamic interactions between the FC and hydrogen storage systems to determine the storage system requirements. The three tasks in the project support the activities in the Engineering CoE to understand the materials operating requirements and transport phenomena in storage systems.
- It is not clear if there are decision points in this project besides the first phase, go/no-go point for the Engineering CoE.
- The combined framework material optimization, fuel cost modeling and vehicle FC system and/or fueling optimization is a good combination of important parameters to help understand the practical potential for MF storage systems on a vehicle.
- University of Michigan should include mass transport into their modeling of packing density and thermal conductivity of MFs.
- The approach is well thought out in terms of material property assessment, material processing and the resulting uptake characteristics, and identifying the decision point before prototyping. Modeling and cost efforts are properly designed.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.9** based on accomplishments.

- This project is still in its early stages. This category may not have relevance at this point.
- This project has been underway for about a year, and work on storage media processing appears to have been limited to a materials database and properties for the selected MOF identified, apparently all taken from the existing literature. Little or no original work on the storage media appears to have been done. Minimal progress on testing design and assembly has been accomplished. Some progress has been made on the modeling tasks that have been accomplished.
- Moderate progress has been made toward elucidating several hydrogen storage issues for FMs, including:
    - Aided in the development of universal modeling framework that embraces vehicle, FC, and storage systems issues;
    - Developed FC waste heat and power models that account for interactions between the H2 storage system and the vehicle propulsion system;
    - Refined their assumptions for the system's component costing matrix;
    - Delivered data sets to the Engineering CoE modeling team for one Basolite, performed property measurements for selected FMs, and initiated a study aimed at reducing variation in critical hydrogen storage measurements.
- Densification studies are just getting started.
- The project's technical accomplishments are consistent with its milestone schedule.
- Five FMs of interest are being surveyed, and data sets of the properties relevant to hydrogen storage are being compiled. The data set for MOF-5 has been compiled and delivered to the other Engineering CoE participants. The selection of a material with which to carry forward has not yet been made. Waste heat profiles for a fuel cell vehicle were assessed, and the required enthalpy of hydrogen release under these profiles has been determined.
- Their progress has been good given the duration of the project to date. The range of uptake for MOF-5, single crystal to loose powder, is quite large and does represent some risk to delivering acceptable processed material

uptake results. Modeling efforts have shown an appropriate level of progress, but the cost effort has yet to get underway.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- Close collaboration with a major MOF manufacturer is critical for this project, but the PIs should keep their options open in this area.
- Having close collaboration with the developers of Lawrence Livermore National Laboratory‘s cryo-compress system may be beneficial.
- Interaction with other Engineering CoE partners appear to be good and working with specific project partner is good. It appears that BASF will play a major role in the project in the media processing task.
- The roles and responsibilities of the project’s partners and collaborators were clearly spelled out in the presentation. The flow of modeling results and performance data to the Engineering CoE seems appropriate. Considering there are three primary partners plus the Engineering CoE partners, the annual funding seems pretty lean.
- It is recommend that the PIs’ collaborations include Omar Yaghi's group from the University of California, Los Angeles.
- Collaborations are strong among the members of the Engineering CoE. The automotive partners are providing guidance to the researchers regarding the applicability of the approaches to the automotive market.
- This is a very good team of collaborators. The addition of UM for their task on framework materials will be valuable to the overall project.
- The participating organizations’ roles are well defined and seem appropriate.

Question 5: Approach to and relevance of proposed future research

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

- Plans for future work appear to be reasonable and consistent with this project's role in the overall CoE's plan for future work.
- The project planning is sharply focused and has been carried out in a logical manner. The decision points are included in the work plan. Barriers to the realization of the proposed technology are being addressed in a seemingly unbiased and independent manner. The risk is mitigated by providing alternate development pathways.
- It will be interesting to see what densification does to FMs and whether the unit’s cell-level structure is robust or whether the nano-porous framework will collapse. Also, hopefully, the binder volume and weight fractions won't be too large.
- The project team should include close interaction with synthetic and process chemists to consider other optimization schemes at the level of MOF product synthesis.
- The future work should include characteristics and operating requirements for promising FMs. If that is successful, the modeling component should provide the dynamic requirements for storage systems that have the potential to meet DOE targets.
- Information regarding the schedule of activities for this project was not presented. A high-level schedule should be provided, at least.
- The densification of FMs is very important for this project.
- The work plan has an appropriate work flow and decision points, and it shows a good balance between technical and cost target assessments.

Strengths and weaknesses

Strengths

- This project comprises a strong technical team.
- The project team has members with strong automotive experience and background.
- Strong materials expertise is coming from a project partner.

- The approach based on a fuel-cell dominant system solution is good.
- This is a strong team with well-integrated partnerships and a sufficient understanding of the barriers to reach correct conclusions about the viability of FMs.
- The project offers very well-defined goals and activities.
- The project addresses at least three areas toward developing commercially-viable hydrogen storage systems.
- This project focuses on physisorption systems, in particular MOFs, and does not attempt to diversify itself too much on other material systems.
- This project has a strong team experienced in framework materials and in dynamical modeling of FC systems. Its activities are focused on providing information in support of the phase one go/no-go decision.
- The overall team is a strength. The overall approach and interrelationship of the tasks is also a strength.
- This is a well-designed program plan with a good balance between technical and cost assessments.

Weaknesses

- Progress on assigned tasks needs to be accelerated to ensure that this project contributes to the overall Engineering CoE goals and objectives.
- It is not clear where this project goes if the chosen FMs fail any of the litmus tests for phase two viability.
- Their approach needs to include material optimization at the level of synthesis, not only material processing and/or compaction.
- The baseline data also needs to include adsorption and desorption kinetics that are measured according to a standard geometric configuration.
- A specific material has not been selected.
- Future work extending out to 2014 was not well defined.

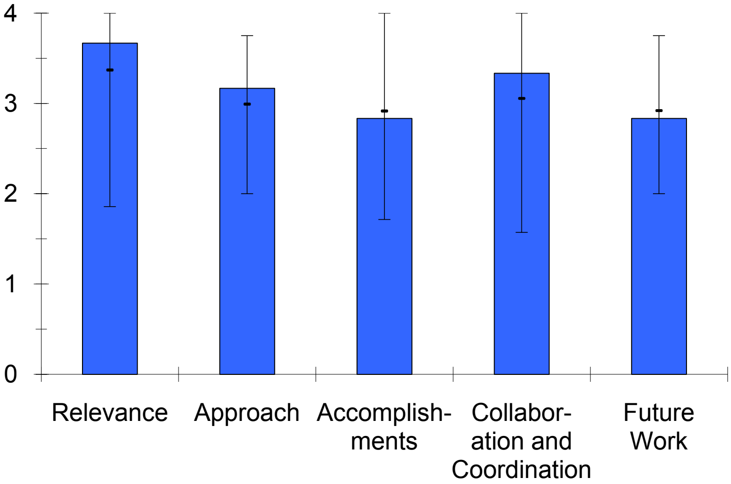
Specific recommendations and additions or deletions to the work scope

- The hydrogen storage capacity of the compacted pellets needs to be validated and compared to the bulk media capacity, before compaction, as soon as possible.
- In this project, there are three tasks, three major partners, and numerous other collaborators within the Engineering CoE. Assuming only the three major partners receive the indicated funding, a figure judged to be about a $500,000 per year total, there would be less than $200,000 per task. In this day and age, that doesn't buy many labor hours in industry and at national laboratories. There is concern that this project and numerous others like it linked with the Engineering CoE are going to have a hard time making significant progress in the many task areas they propose to address.
- They should revise their approach to include material optimization at the level of synthesis.
- The project team should develop a plan to gather baseline kinetic data for MOFs.
- It is recommended that the PIs study, or show the relationship among, dormancy – a full cryo-MOF tank sitting for weeks – insulation, environmental temperature, and any hydrogen venting from cryo-tank systems designed for given MOFs.

Project # ST-11: Fundamental Reactivity Testing and Analysis of Hydrogen Storage Materials

Don Anton; Savannah River National Laboratory

Overall Project Score: 3.1 (6 Reviews Received)



Brief Summary of Project

The objective of this study is to understand the safety issues regarding solid state hydrogen storage systems through: 1) developing and implementing internationally recognized standards for testing techniques to quantitatively evaluate both materials and systems, 2) determining the fundamental thermodynamics and chemical kinetics of environmental reactivity of hydrides, 3) building a predictive capability to determine probable outcomes of hypothetical accident events, and 4) developing amelioration methods and systems to mitigate the risks of using these systems to acceptable levels.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.7** for its relevance to DOE objectives.

- This project is crucial for hydrides-based hydrogen storage, especially for the systems based on air- and/or moisture-sensitive, complex hydrides.
- This project addresses several of the safety issues for representative solid materials used for hydrogen storage. It combines empirical test procedures with model simulations for a couple of the more probable accident scenarios. Some possible mitigation methods that potentially reduce flammability and water reactivity hazards were proposed, although those were not explicitly identified during the AMR presentation, and initial behavior of the treatments with typical hydrides were assessed. Savannah River National Laboratory (SRNL) made relative comparisons of trends in reactivity with air, water, and other fluids found in vehicles on a few materials they considered to be representative. However, their choices were clearly not extensive.
- A comprehensive understanding of safety issues associated with solid-state hydrogen storage systems and the development of accident mitigation strategies are vital to the successful deployment of H_2/fuel cell systems using these storage media. This project addresses important safety issues in the use of several promising solid-state storage materials. System safety is recognized by the DOE as a critical element of the total Hydrogen Storage Program. This project comprises experimental testing, modeling, and risk mitigation strategies that fully support the DOE's program objectives.
- The safety of hydrogen storage media is of paramount importance.
- This project helps to fill an important niche in the practical understanding and use of solid-state hydrogen storage media, namely reactivity and safety.

Question 2: Approach to performing the research and development

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

- The basic water-drop tests are fine for establishing a baseline understanding of these materials. The PI has made efforts to study these materials under more pertinent system conditions, for instance, in pelletized form. The focus of the project really needs to shift to achieving a better understanding of how these materials will actually be packaged in a system, and how they will be released in the case of a tank failure. It is critical that this project is closely linked toSandia National Laboratories' (SNL) ST-013 projects – the reactivity properties of hydrogen storage materials in the context of systems – for guidance.

- The approach is quite good. However alane (AlH_3) was tested for material prepared by only one method. The tested material contained metallic aluminum, which is pyrophoric and highly air sensitive on its own. Also, U.S. Department of Transportation (DOT) testing is missing.
- Most of the materials screening assessments of reactivity were qualitative to derive trends and relative rankings for a few metal hydrides, ammonia borane (AB), and activated carbon. On the other hand, various quantitative models were formulated to stimulate a couple of simplified accident conditions. While response of the tested materials to standard safety tests does confirm the greater potential of hydrides to cause more damage than the carbon or AB, the mitigation methods do offer some expectations for safer behavior upon water exposure or powder dispersion during an accident. These materials may all be too reactive to satisfy vehicle safety requirements.
- The approach comprises materials testing, model development, and risk mitigation tasks. The approach is straightforward, and it is being employed to understand the mechanisms of ignition and to test strategies for accident mitigation. Good communication with the materials CoEs is apparent; this is ensuring that the most promising candidate materials are being tested in the project.
- Standardized test procedures are being employed. Mitigation strategies are being pursued.
- Reactivity testing of candidate hydrides and hydride mixtures is greatly needed. This need is being filled here.
- The thermodynamic model to predict possible ignition from combustion and dehydriding heats of reaction, as well as other physical properties, will be very useful.
- Mitigation efforts are centered around the pelletizing of the storage media with the simultaneous addition of retardants, which is a good approach.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- The PI established a good baseline data set of the material properties.
- It would be good to have some more information on the basic premise of the mitigation techniques and relative pros and cons as soon as possible. Is it similiar to the polystyrene work conducted by the SNL project? If not, what are the different mitigation strategies?
- The results on AlH3 are very incomplete. Taking into the consideration the high profile of this project and the fact that it is close to completion (90%), it will be a great disappointment if it ends before all the tests are performed. In general, the presenter has not shown too much progress for a five-year project.
  Most of the testing results for water and air exposure of the metal hydrides were done on as-prepared samples from limited (i.e., one or two) sources. It would have been much more valuable to have also assessed the behavior of cycled and desorbed materials, which are often much more reactive and sensitive to the environment. The rankings are really of limited scope. The amount of effort required to develop and to extend the simulation models for the hydrides and AB appear to have only limited value. They considered this to be rather ideal processes that may not be typical for real accidents. These models did apparently suggest some means to control the reactivity.
- Good technical progress has been achieved on the testing and modeling tasks. However, given the considerable amount of information that already exists about the ignition properties of alane upon water exposure, it is surprising that so much effort was devoted here to that work. Comparisons should be made with prior work on alane reactivity. Also, the testing of reversible storage materials should be made after several sorption cycles to determine if the reactivity of the cycled material is the same as for the starting material.
- Modeling results that were obtained regarding the ignition characteristics of $2LiBH_4/MgH_2$ as a function of pellet size are especially intriguing, and they suggest a compelling pathway to mitigate accident risk. Unfortunately, proprietary technology issues limit the extent to which the four proposed mitigation strategies can be understood and reviewed.
- The studies of ignition properties of AB were initiated in this project in 2009. The work in 2010 on cylinder self-heating is a useful extension of the earlier work, and it provides important new information that can be used in the risk analysis of systems that may employ this promising candidate material.
- The ignition and reactivity properties of only one type of alane (from SRNL by Zidan, et al., slide 7) are being studied. However, the presenter contended that there were differences that depended on AlH3 synthesized in

different ways. That needs to be definitively demonstrated. Also, the ignition behavior for powder scale as a function of the size and/or quantity of material is needed to make contact with practical applications.
- There are significant safety issues with water reaction of alane that have been identified.
- Quite a lot of reactivity data has been obtained on several candidate hydrides. It has been clearly shown that there can be substantial variations among various materials.
- Is a particle size of 40 nm much too fine for alane? Many metal powders, especially Al, would be hazardous at that particle size.
- SRNL seems to have developed a viable risk mitigation approach using pellets and additives that reduce reactivity. There is little detail because of pending patent disclosures. At least, it would be useful to know how much the gravimetric density is reduced by the incorporation of a presumably inert additive.
- The pellet model promises to be very useful.
- The United Technologies Research Center (UTRC) talk (ST-012) also uses a pelletizing approach. It is not clear how the SRNL mitigation approach differs from UTRC's.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- The level of coordination has improved through the years especially now that it's part of the Engineering CoE.
- More consultation with the OEMs is still needed to understand how these materials will behave in a real automotive environment.
- This project exhibits good collaboration that is quite sufficient for such a project.
- There were substantial technical interactions of SRNL with other safety projects at SNL and UTRC, as well as with the international hydrogen storage research community. This appears to have been of benefit to all parties.
- Good collaboration between SRNL and the material CoEs in selecting the most promising materials for further study is evident. Close collaboration with selected partner organizations is apparent, especially in the areas of pellet size effect modeling (SNL) and ammonia borane cylindrical modeling (PNNL). However, noteworthy contributions in 2010 from other partners from Forschungszentrum Karlsruhe (FZK) in Germany, the Université du Québec à Trois-Rivières (UQTR) in Canada, and UTRC are not evident from this presentation. A chart showing roles and responsibilities of partner organizations would have been useful.
- There is a good level of interaction with other institutions.
- The collaborations seem to be especially good, including the international ones within International Partnership for the Hydrogen Economy (IPHE) and International Energy Agency Hydrogen Implementing Agreement (IEA-HIA).

Question 5: Approach to and relevance of proposed future research

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

- The focus of the project really needs to shift to achieving a better understanding of how these materials will actually be packaged in a system, and how they will be released in case of a tank failure. Questions of interest include:
    - What is the real spray pattern if the system depressurizes?
    - How much hydrogen is coming out, and what is the true particle size and distribution?
    - What binders, mitigators, and initiators are involved?
- Lithium-ion batteries can be flammable, but appropriate packaging techniques are employed as mitigation techniques. This project should look at it from the same perspective and understand how it looks in the system first before testing its properties. Heavy coordination with SNL (ST-013) is required.
- The proposed work section is too short. It is not clear what is planned to fill all the remaining gaps in a short period of time.
- The tasks identified to be performed prior to the end of the project by October 2010 appear reasonable and would provide at least some measure of completeness. It would be more helpful to the hydrogen storage and engineering teams for SRNL to assess more thoroughly the mitigation methods that apparently have had relatively limited evaluations. It is not so obvious that completing the phase three

modeling efforts would contribute significantly greater insights on the safety characteristics of the materials. Also, it is unclear how much progress can be made with the newly purchased high-pressure differential scanning calorimeter in the next two to three months remaining for this project. That is, unless this capability would be directly applied to the Engineering CoE work at SRNL.
- The future work represents a clear extension of ongoing work in 2010. However, it is not apparent whether any new materials identified by the CoEs and independent projects will be tested. Future work should include a study of the reactivity as a function of pellet size and sample volume.
- This project will end in September 2010 and is in a windup mode.
- It will continue as planned. The contract will end soon.
- Should there be specific go/no-go downselections soon for materials that are shown to be especially hazardous?

Strengths and weaknesses

Strengths
- As already mentioned, this project is crucial for metal hydride-based hydrogen storage, especially for the systems based on air- and/or moisture-sensitive materials.
- The major strengths of the project include a combination of experimental tests and modeling as well as a broad collaboration with others.
- A fairly diverse group of hydrogen storage materials were subjected to basically identical safety screening tests for water and air reactions to give a relative ranking. The concept of combining experimental tests with detailed modeling to simulate chemical reactions during possible accident conditions is attractive and should be followed in future safety evaluations. Using the results from modeling to develop mitigation methods does provide a more efficient means to improve safety.
- This is one of the few projects in the Hydrogen Storage Program that is devoted to the important issues of materials safety, risk assessment, and risk mitigation. The SRNL engineering team and their partners are well qualified to conduct this work, and solid experimental testing and modeling efforts are underway.
- The project team's focus is on the important safety-related issues.
- They have shown good, practical testing and modeling.

Weaknesses
- Taking into consideration the high profile of this project, it will be a great disappointment if it ends before all the materials selected are properly tested.
- There was no explanation for why the DOT tests are missing.
- Many of the screening tests are qualitative and difficult to systematically reproduce. Also, assessment of any storage material should have included tests on depleted and partially reacted materials before drawing conclusions on relative stability and reactivity of the prepared materials alone.
- It is not clear how the material ignition characteristics scale with the sample size. Only small samples were tested here. An analysis that extends the results to real-world sample sizes is needed.
- None.
- All the reactivity scenarios cannot be covered.

Specific recommendations and additions or deletions to the work scope

- Complete the tests and include the DOT tests.
- It is recommended that the project team use the remaining time in this project to assess the possible effects of the mitigation methods to improve materials safety. Complete the materials characterizations and include evaluations of cycled and/or depleted materials.
- A comparison of ignition results with data from prior studies would be useful.
- Specifically, a thorough review of previous work on alane ignition characteristics and mitigation strategies is needed. The results of this project should be examined within the context of work that has already been done on alane and other metal hydrides.
- None.

- Be prepared to add new, promising materials that might come from the DOE CoEs and other independent hydrogen storage materials R&D.
- The PIs should consider redoing the alane work with a more reasonable, coarser particle size.

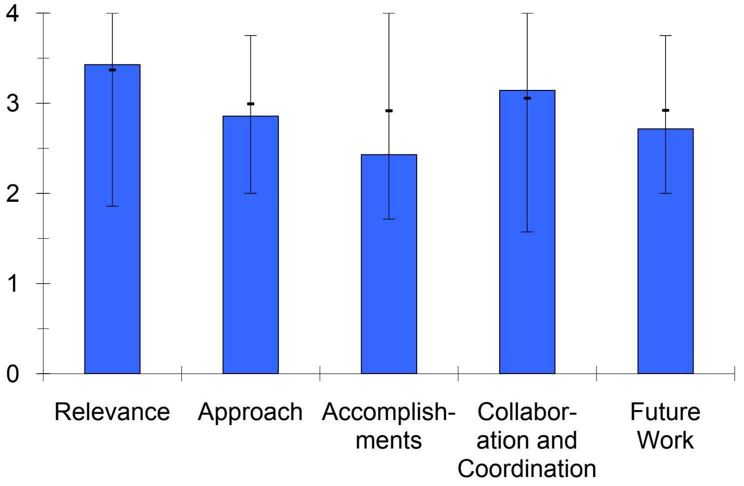
Project # ST-12: Quantifying & Addressing the DOE Material Reactivity Requirements with Analysis & Testing of Hydrogen Storage Materials & Systems

John Khalil; United Technologies' Research Center

Brief Summary of Project

The high-level objectives of this project are to: 1) contribute to quantifying the DOE on-board storage safety target of meeting or exceeding applicable standards, 2) evaluate reactivity of key materials under development in the materials CoE, and 3) develop methods to assess and reduce risks. The primary tasks include: 1) risk analysis, including qualitative risk analysis (QLRA) to develop a broad range of scenarios and quantitative risk analyses (QRA) for key scenarios, 2) dust cloud material testing with standard and modified American Society for Testing and Materials (ASTM) procedures, reaction kinetics material testing for air exposure and/or time resolved X-ray diffraction, 4) material-based risk mitigation, and 5) risk mitigation for subscale prototypes.

Overall Project Score: 2.8 (7 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- The project supports the Hydrogen Storage Program and the DOE's goals and objectives. It is an important component of the materials evaluation process.
- This project addresses accident risk factors and the probability for accidents with respect to the safety of on-board hydrogen storage system based on solid media. Nearly all reported efforts were for metal hydrides, specifically $NaAlH_4$. Extensive effort was shown in fault-tree analysis for a specific accident scenario with a metal hydride. However, little attention seemed to be given to other media such as activated carbon adsorbents or ammonia borane (AB). $NaAlH_4$ beds as analyzed are very high safety risks with only minimal attention apparently given to potential mitigation schemes. An experimental assessment of powders during "blow down" testing could be useful in rating relevant risks of different storage materials.
- Finding safe and compact ways to store hydrogen is very relevant to DOE's goals. The data obtained through the materials tests and prototype testing in this research should be very useful in determining which materials to use for hydrogen storage.
- A quantitative analysis of risks and failure modes for a range of hydrogen storage scenarios, and an assessment of risk mitigation strategies are vital to the hydrogen program. This project is directly relevant to DOE objectives.
- This risk assessment study is highly relevant to the safety of hydrogen storage systems.
- This project directly addresses DOE objectives to evaluate and mitigate safety aspects of hydride storage tanks.
- It is a needed and critical effort to establish whether solid-state materials are safe to use in public hydrogen transportation scenarios.

Question 2: Approach to performing the research and development

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

- The PIs presented a reasonably good combination of theoretical and experimental data.
- The primary effort has been the development of qualitative and quantitative risk analysis (RA) models for

reversible storage media, particularly metal hydrides such as $NaAlH_4$, supplemented with some materials characterization and testing of powder flammability and reactivity with air and/or water. Detailed RAs were focused on a limited set of presumed high-probability accident scenarios such as the rupture of a hydride tank or inward leaks of air. While such RAs can be very involved, they are highly dependent on the validity of the input parameters that are usually extremely difficult to determine with accuracy and reliability.

- The quantitative risk analysis, using the event tree model for an external fire or the fault-tree model for in-vessel air leakage, is interesting and should yield some useful results. There are, however, some questions concerning the material reactivity risk mitigation tests on $NaAlH_4$ + 4 mole% $TiCl_3$ that should be addressed. In testing the loose powder, an unspecified amount of water or windshield washing fluid was dropped onto the $NaAlH_4$ causing a fire. Then, when a one-gram "wafer" of $NaAlH_4$ was dropped into 25 milliliters of washing fluid, there was only a mild reaction without flame. How much water was dropped onto the powder, and why wasn't this same procedure used for the wafer? Dropping a wafer into a relatively large quantity of liquid is not the equivalent to dropping some liquid onto dry powder. An identical process should be used for all tests before any legitimate comparisons can be made.
- A risk analysis framework has been developed that includes work on materials testing, modeling, accident mitigation, and prototype testing tasks. The approach efficiently addresses critical safety issues in a straightforward and detailed way. The use of fault-tree analysis methods for accident and risk prediction is a solid addition to the project. However, the accuracy of the results depends strongly on the correct assignment of branch probabilities, and the method for assigning preliminary probabilities is questionable. Experimental studies are largely limited to fast blowdown and/or depressurization tests. However, this addresses only a limited subset of possible accident scenarios.
- There is a need to complement the expert panel with data where possible (e.g. National Transportation Safety Board (NTSB) data for initiating events).
- This presentation needs to be made clearer to the non-specialist audience.
- The relevance of all the experimental efforts to this project was not well understood. Much of it appears to duplicate work being done elsewhere in the Engineering CoE.
- This project seeks to quantify the risks associated with one hydrogen storage system that has already been well studied and characterized.
- Once the system's risk probabilities for various accident scenarios have been calculated, will they be compared to actual system failure tests?
- The project objective is to develop detailed fault-tree analysis models of possible accident events such as rupturens and spills. In that sense, it importantly goes beyond the SRNL project (ST -011) to cover the whole storage system.
- The expert panel should be very useful to this effort.
- Some of the storage media testing and mitigation approaches overlap a bit with the SRNL project, but coordination seems to be largely avoiding overlap (e.g. dust clouds at UTRC versus piles at SRNL). Where there is H_2O contact testing, UTRC seems to be focusing more on $NaAlH_4$, a hydride they have used extensively in prototype tanks.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.4** based on accomplishments.

- The elaborate calculations produced reasonable-looking conclusions. However, the recommendations developed by theorists require an additional review. For example, the compaction of $NaAlH_4$ powder can have a different-than-predicted effect. If exposed to water and/or moisture and oxygen, the material on the surface of the pellet may form a dense crust containing sodium peroxides. This effect could cause serious problems, because they can explode in contact with the remaining metal hydride once the crust is destroyed as the exposed material is removed from the damaged container. The content of peroxides in compacted material may exceed the powder's content where peroxides can be easier eliminated because of the presence of water and metal impurities. This explains the "fair" rating.
- Also, X-ray diffraction results on slide 23 should be normalized to NaCl (sodium cloride) as an internal reference - the NaCl content remains unchanged during the cycling. In such a case, the concentration of $NaAlH_4$

does not increase with cycling. On the contrary, the concentration of trisodium hexahydroaluminate (Na_3AlH_6) does slightly increase. Apparently, the chemistry of cycling experiments requires an additional evaluation.
- While UTRC has performed an extended RA fault-tree simulation for the in-leak of air into a hydride bed, this is just one of various potential accidents, each with different weighting factors. Without a support test matrix assessment, it has really limited predictive capability for vehicle accidents and safety. Most measurements of reactivity appears to have been performed on $NaAlH_4$ and not other types of solid storage options. The development of a blowdown test facility looks like a potentially useful tool to assess the behavior of various materials during the remainder of the project.
- A good presentation of the various approaches used to evaluate, quantify, and assess risk is given. However, there are relatively few results. There are some results for the material reactivity risk mitigation tests on $NaAlH_4$ + 4 mole% $TiCl_3$, but no results are presented for tests done in the fast depressurization apparatus. The results on the simulations are interesting and could be useful.
- Although the fault-tree analysis is a useful protocol for assessing accident initiators, the results are difficult to understand based on the information provided in this presentation. The principal results of the fault-tree and sensitivity analyses, as well as the stochastic simulation results, need to be presented in a clear, concise way. Also, all branch probabilities in the fault-tree analysis are presently stated as being preliminary. However, the assignment of probabilities based solely on the advice from experts is flawed. Since the credibility of the entire analysis can be traced directly to the accuracy of those probability assignments, a much more careful and quantitative approach is needed. What approach will be used to assign final probability values?
- The fast blowdown and depressurization approach for assessing results of accidental breach of the hydride reaction vessel can potentially provide important information. However, results from those tests weren't presented. Results on the cycling of $NaAlH_4/TiCl_3$ are presented after the description of the fast blowdown test system. These results have been presented previously by other investigators, yet there is no apparent relationship to the blowdown studies. It is not clear why those results are presented here.
- The model is developed and the probabilities are populated.
- How are results from the experimental work incorporated into the risk assessment analysis?
- The project's progress has been good.
- The fault-tree model seems to have been developed with much detail and rational thought.
- UTRC is in a good position to start the important dust cloud tests soon..
- The pelletizing work has been very useful and practical. There may be a little overlap in this area withSRNL.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- The project involves an outstanding group of experts. However, a collaborator with chemical expertise may strengthen the team and the project.
- UTRC has interacted with several organizations regarding safety issues, risk testing, and materials properties. These appear to have been of mutual benefit. It would be good if the safety data from UTRC can be communicated to the organizations involved with developing codes and standards for hydrogen storage and fuel cells.
- There is evidence that this group has active partners and collaborations both within and outside the CoEs. These seem to be appropriate and should continue.
- Although many collaborators and expert panel members are listed, their specific roles and what they actually did on the project are not apparent from the presentation. The involvement of Kidde-Fenwal on dust cloud testing is an important addition to the project. However, only limited results are presented.
- The PIs need to involve other partners, like OEMs and NTSB, in the risk assessment effort.
- Why is there no OEM involvement?
- The project team's collaboration with others has been excellent and well focused.
- Communication with the other two DOE reactivity laboratories, SNL and SRNL, seems to be adequate.
- Many other good collaborations including international organizations IPHE and IEA-HIA are included.

Question 5: Approach to and relevance of proposed future research

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

- It is strongly recommend that the project team do experimental testing only after a reality check of theoretical results.
- UTRC has identified two primary tasks to perform during the project: 1) Continue to develop and expand the RA methods for reversible hydrogen storage and 2) conduct various reactivity experiments and characterization using the blowdown test facility. It was not clear how many different materials and their variations based on source and processing conditions can be assessed during the remainder of the project. The later work is probably much more valuable to the DOE Hydrogen Storage Program.
- In particular, risk model simulations are highly dependent on input assumptions and relative probabilities for different scenarios.
- The work that is planned seems appropriate. The tests that are planned on material and system testing and mitigation have already begun and should continue. The quantitative risk analyses on accident sequences are also appropriate.
- The future work is a continuation of the technical effort currently in place. A risk analysis for off-board regeneration is an important addition. A more definitive and quantitative method for assigning branch probabilities is needed to ensure that the analyses are credible.
- This work needs to focus more on developing realistic probabilities for events by seeking external data rather than relying on an expert panel.
- The project's future plans look good.
- Most of the PIs' future efforts listed will be clearly useful.
- The value of $NaAlH_4$ developed from past prototype experience is understood, but it seems this material has a spectrum of problems, including safety that suggest it should be abandoned in favor of more promising, modern alternatives.

Strengths and weaknesses

Strengths

- Having a good combination of theory and experimentation is a strength.
- Another strength is the combination of detailed, formal RA simulations of accident scenarios with performing selected materials reactivity under various conditions.
- The fast blowdown depressurization rig is well designed and should eventually produce some useful data.
- UTRC has considerable experience and expertise in hydride system safety issues, analysis of system failure modes, and exploration of mitigation strategies. Properly applied, the fault-tree analysis is a useful way to examine various accident scenarios.
- The model is developed.
- The system risk probability approach is interesting.
- The project's research includes past material and prototype experience.
- The project shows good engineering and statistical abilities.

Weaknesses

- The project is weak on the chemistry side. It is strongly recommend that the PIs involve a chemistry partner(s) into the safety tests design.
- The RAs are susceptible to subjective assignments of various risks and their probabilities that are often very difficult to validate. Only a limited number of accident scenarios were actually evaluated in detail.
- The approach used to compare the material reactivity risk mitigation tests on $NaAlH_4$ + 4 mole% $TiCl_3$ should be re-evaluated to make sure that all comparisons are being made under similar conditions.
- Only limited information is supplied about how probabilities are assigned in the fault-tree analysis, and how uncertainties in those probabilities are determined. This information is critical in establishing the viability of the analysis.
- So far, the experimental efforts are the project are extremely limited. At this stage of the project (about 65% complete), it is expected that the experimental work would be further along, especially since it is apparently being used to provide input to the quantitative studies on the project.
- There is a lack of validated data for model.
- The project team needs more experimental data to assign risk probabilities to each individual event.

- None really significant.

Specific recommendations and additions or deletions to the work scope

- It is recommended that the UTRC limit further detailed RA simulations on various accidents, and instead prepare thorough documentation on their approach and results obtained to date. This information should be archived with the DOE and made available to the general hydrogen fuel cell R&D community.
- It is suggested that UTRC concentrate on performing the blowdown tests on $NaAlH_4$ and as many other materials as possible. Also, the tests should be performed on samples of cycled and depleted materials, as these are often much more chemically reactive than starting hydrides.
- The PIs need to provide more detail about the assignment of final probabilities and uncertainties in the fault-tree analysis. A risk assessment of the fault-tree procedure itself is needed. The team should accelerate experimental work using the blowdown and depressurization system.
- They should incorporate real data into the model.
- This project needs more emphasis on risk mitigation based on experimental work.
- The PIs should consider terminating the $NaAlH_4$ work in favor of other, newer materials.

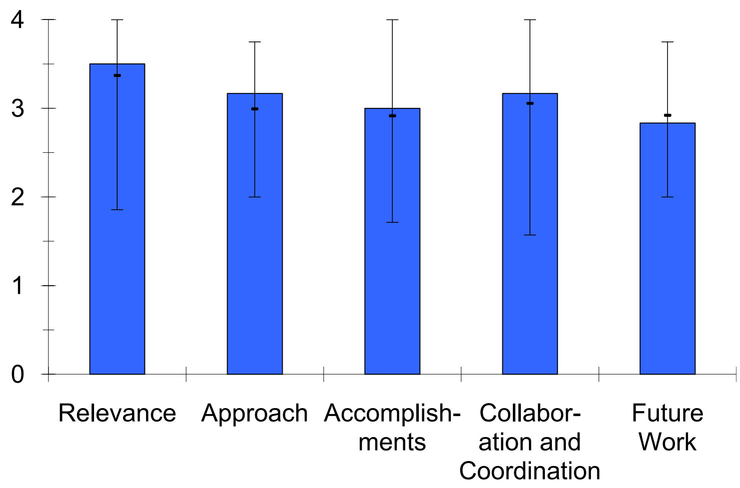
Project # ST-13: The Reactivity Properties of Hydrogen Storage Materials in the Context of Systems

Daniel Dedrick; Sandia National Laboratories

Brief Summary of Project

The overall objective of this project is to understand the behavior of hydrogen storage materials and systems in preparation for deployment. The objectives are to: 1) enable the design, handling, and operation of effective hydrogen storage systems for fuel cell applications, and 2) provide a technical foundation for eventual codes and standards (C&S) efforts.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Gaining knowledge of the environment and conditions under which materials will be exposed is critical to understanding how to design systems for safety and performance.
- New materials can't be used for practical applications unless they are safe. So, the focus of this project on the safety of hydrogen storage materials is obviously very relevant to DOE objectives.
- Understanding and optimizing the behavior of solid-state metal hydride materials in an operational fuel cell environment are important components of the overall Hydrogen Storage Program. This work directly supports DOE RD&D objectives.
- The materials being tested have little chance of commercial use. Although the methods developed may be used for commercial materials, the experiments will have to be repeated.
- This project is focused on the safety of hydrogen storage material systems.

Question 2: Approach to performing the research and development

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

- The project's overall goals are appropriate and on track.
- The PI should also consider how material packing in different support structures and thermal management equipment will affect their release and properties, for instance are the materials packed in a honeycomb structure as proposed by Savannah River National Laboratory's (SRNL) ST-011 or in an aluminum mesh such as Van Hassell's project ST-006?
- The project is well thought out and is organized into three tasks: characterize behavior, consequence analysis, and mitigation strategies. The first and second tasks represent a good approach. However, using the mitigation methodolgy in the third task is strongly dependent on materials properties that could vary widely. So, it's recommended that the PI not use this materials-based approach within this project.
- The experimental methods are sound and should continue. The residual gas analyses should also be incorporated into the project to test for gaseous decomposition products.
- A broad-based approach encompassing system design and definition, characterization of material behavior, hazard and consequence analysis, and risk mitigation and accident prevention has been adopted. This provides a solid, nearly end-to-end examination of critical elements that enable the future deployment of metal hydride storage technologies.
- Their modeling efforts are a good contribution that will be applicable to future materials and systems.
- The focus is on identifying mitigating strategies for high-risk scenarios in selected metal hydride materials.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- The project shows good progress, especially in developing mitigation materials such as the polystyrene mixes. The PI should determine if these materials will be stable in high-temperature environments. Obviously, these approaches need much more investigation to understand issues such as material compatibility. Such work should be coordinated with SRNL's ST-011 project.
- Some useful results have been obtained. Mitigation of sodium alanate ($NaAlH_4$) was attempted through the use of a polystyrene matrix. The results indicated that the mitigated samples were less reactive than the neat samples. Cycling studies resulted in no loss in activity of the $NaAlH_4$. Results indicate that it might be possible to tailor the matrix. The results are interesting, but it might be useful to try some other matrices for comparison.
- The project shows good modeling results on fire impingement and over-pressure scenarios. However, at this stage of the project, which is about 75% complete, at least preliminary experimental results that test the models are expected. There is excellent work being done on development of new mitigation strategies, such as heat shielding and incorporation in a matrix, for various accident scenarios.
- Matrix material work is especially interesting and innovative, however some important issues about the addition of composite matrix materials should be addressed in greater detail. Specifically, a close examination of structural changes that occur in the matrix when it is heated above the glass transition temperature would be useful to understand matrix-hydride interactions. Specific questions still to be answered include do temperature excursions through the glass transition temperature affect the sorption properties of the hydrides and what is the dependence of the structural morphology of the matrix on the concentration of a cross-linked polymer (i.e., is there an optimum concentration for which the matrix structural integrity is maintained while limiting the volumetric and gravimetric penalties imposed by the addition of the polymer).
- Using mitigation strategies, such as heat shield and polymer matrix, are likely to be applicable to future materials.
- The results given on the metal-hydride and polymer composite materials look promising.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.2** for technology transfer and collaboration.

- Working in the Engineering CoE, the project team will continue to consult with OEMs to understand the true operating environment of these materials.
- Since this group is a part of Sandia National Laboratories (SNL), they have ample opportunity for collaborations and have a number of partners and collaborators, as expected.
- More visible collaboration with the other related projects would be helpful since it appears there is an overlap with SRNL project's mitigation approach.
- Having close collaborations with experts in partner institutions directly complement and support the SNL's modeling and experimental work. It is recommend to foster closer collaboration with the Engineering CoE.
- The project exhibits a good variety of partners, but there was little information given on the actual contributions of these partners.
- It is not clear how extensive is the interaction with the SRNL safety project.

Question 5: Approach to and relevance of proposed future research

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

- It is not clear whether a 100-g sample size will be sufficient to truly understand how these materials will behave in a thermal or kinetic event.
- The plans to focus on mitigation and the development and characterization of new materials seem appropriate. This project builds on past accomplishments and is a logical next step. The investigators should do residual gas analyses on the mitigated samples to test for decomposition products.
- Focusing on using the mitigators represents a weakness as they are, again, a strong function of the material properties.

- The future work focuses on optimizing mitigation methodologies and strategies. Given that the project is nearly complete, this is a prudent decision. It is recommended that a more indepth assessment be conducted on the structural and chemical changes that may occur in the polymer-hydride matrix upon temperature cycling of the system. Also, additional efforts directed toward experimental validation of the modeling work is needed.
- The mitigation focus is good. Mitigation strategies should aim for general methods that may be applicable to real systems rather than specific to current model materials.
- This project ends in September 2010. Its future work will emphasize optimizing metal hydride and polymer composites.

Strengths and weaknesses

Strengths

- There are a variety of collaborations and partners that should add strength to this project. The concept of mitigation is a sound one that should yield useful results once an appropriate matrix is identified.
- This is a very good team with strong capabilities.
- The project team is extremely capable and well qualified team. There are innovative mitigation strategies being developed.
- Their modeling activities are strengths.
- The project team's work in developing potentially useful risk mitigation approaches for metal hydrides is a strength.

Weaknesses

- In the mitigation tests, a polystyrene matrix was utilized without the investigators knowing what effect it might have at temperatures in excess of 100 ºC. The investigators should assess the effects of the matrix on the mitigation experiments before going any further. Results of this have been presented at several research conferences, but there is no evidence of any publications in refereed journals this past year.
- The project is starting to take on the materials modification approach in order to improve safety. This is somehow taking the project away from its engineering-based approach.
- Clarification of the project role and what differentiates it from other projects withing the Metal Hydride Center of Excellence researching the safety of handling H_2 storage materials would be helpful.
- Experimental validation of the models is lagging. A greater focus on validation is needed. Presentation of technological challenges and obstacles to deployment of heat shielding and matrix incorporation approaches for material risk mitigation is lacking. A quantitative analysis of changes in hydride and matrix material properties upon temperature cycling is needed.
- The mitigation approaches identified may not be applicable to a wide range of metal hydrides. Polymer decomposition issues should be addressed to a greater extent.

Specific recommendations and additions or deletions to the work scope

- Keep the project. However, it is recommended to refocus the third task on finding engineering solutions rather than materials-based solutions, for instance, delete using mitigators.
- A more complete description and discussion of the obstacles and hurdles faced in deployment of heat-shielding and matrix materials for accident mitigation is needed. Also, a more detailed examination of chemical and structural changes that occur in the polymer-hydride matrix during sorption reaction cycling should be performed.
- It is recommended that the PI develops stronger ties with the Engineering CoE.
- None.

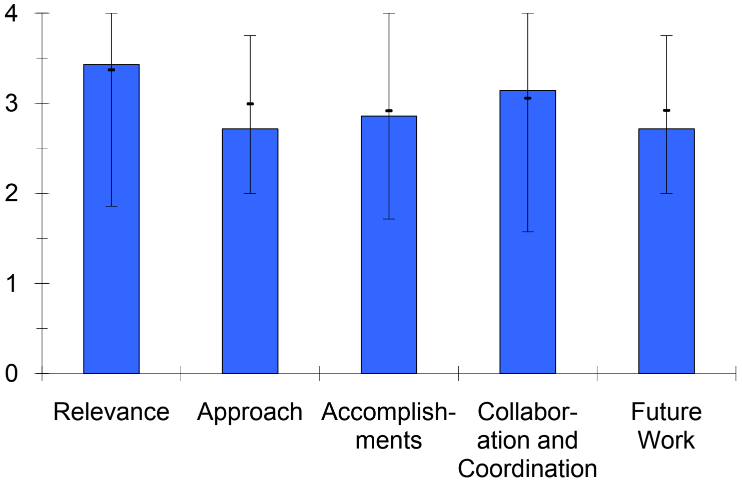
Project # ST-18: A Biomimetic Approach to Metal-Organic Frameworks with High H_2 Uptake

Hong-Cai Joe Zhou; Texas A&M University

Brief Summary of Project

The ultimate goal of this project is to prepare a metal organic framework (MOF) hydrogen sorbent material with both high surface area and high hydrogen affinity. The objectives for 2010 are to: 1) construct MOFs containing mesocavities with microwindows that may serve as a general approach toward stable MOFs with higher surface areas, 2) incorporate entatic-state metal sites into the high-surface area MOFs, 3) design and synthesize porous organic frameworks (POF) for hydrogen storage with high surface area, tunable pore size, and flexibility, and 4) determine H_2 adsorption of POFs doped by metal, such as lithium (Li) and nickel (Ni).

Overall Project Score: 3.0 (7 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- The objective of this project is to design, synthesize, and characterize MOFs with active metal centers aligned in porous channels and accessible by hydrogen molecules.
- This project is innovative and aligned to key goals with high risk, which is appropriate.
- This project is targeted at developing a MOF material with high hydrogen capacity at room temperature.
- The project's objectives are well-aligned with the Hydrogen Storage Program and the Hydrogen Sorption CoE (HSCoE).
- Exploring new MOF and POF adsorbents with ambient operating temperatures and high storage capacities is an important research activity in reaching the ultimate performance target.
- In general, the project goals are focused on the hydrogen storage DOE program objectives in relation to rapid discovery and characterization of novel sorbents. The intended focus of this project appears to be appropriately focused on augmenting gravimetric capacity and binding energy, although not enough emphasis or consideration was given to volumetric capacity. Perhaps that is the most challenging target for this class of materials.

Question 2: Approach to performing the research and development

This project was rated **2.7** on its approach.

- The PI needs to consider sorption enthalpy and the practical aspects related to packing and engineering system design. High surface area is only one part of the solution, and all the tradeoffs must be considered.
- The PI is unnecessarily insisting on high surface area materials knowing that this could be done only at the cost of volumetric storage density. He should put some effort on the other half of the project, which is to increase binding energy.
- This project exhibits good guiding principles.
- This project team may benefit from thinking about how the system would work if they accomplished the desired geometry and storage.
- The stabilities of different MOFs being pursued was not discussed.
- The systematic approach of synthesis and structural characterization of the new materials is sound.

- However, the PI should deemphasize aiming for high surface area as a main goal of the project. It should only be thought of as one approach to increase capacity, keeping in mind the likely tradeoffs in material stability and cost. Besides, it is doubtful that obtaining high surface area alone is the right path toward the ultimate storage capacity. Instead, the goal for higher heats of adsorption should be given more effort.
- The approach of this project was described as biomimetic, although it is not clear how these MOFs are biological in nature. The approach and materials seem to be identical to that taken by other MOF-projects and/or researchers (i.e. mixing traditional metal salts and linkers). Most of the prepared materials involve paddlewheel clusters which are already common in the MOF literature, and so the biomimetic spin seems a bit strong. Perhaps the biomimetic spirit of this project should be deemphasized if it is not being truly adopted.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.9** based on accomplishments.

- It would have been useful to look at the delta-H [enthalpy heat of adsorption] for various materials as well.
- Moreover, the main purpose of the project is to show the benefits on hydrogen adsorption of having open metal centers in the adsorbent. Unfortunately, this is not clear after three years of effort.
- The project is making very good progress. Reproduction [of measurements] outside was important.
- The formation of MOFs with the highest surface area is very good; however, it will not allow for acheiving the DOE targets given its low volumetric capacity and low heats of adsorption.
- Though the main idea is to enhance the heats of adsorption using open metal centers, the project seems to be diverging from its main concept.
- The best result thus far is the 7.2 wt.% (percent by weight) hydrogen in PCN-68 (porous coordination network [Zhou group designation]) at 77K and 40 atm.
- The number of new ligands and corresponding adsorbent structures discovered is a significant achievement.
- Important progress was also made toward understanding of these new types of MOFs and physical properties.
- The researchers clearly have a strong aptitude for rapidly preparing and characterizing new MOF materials and corresponding linkers. The characterization also seems appropriately focused on determining hydrogen capacity and isosteric heats. More emphasis and data on volumetric capacity should be included in the future. The PI mentioned obtaining a device to measure density; however, one can easily determine loose powder density in the laboratory for preliminary reporting. This volumetric issue is particularly important for this project since they appear to be interested in preparing MOFs on very expanded linkers, spanning 4+ phenyl rings. It is anticipated that MOFs based on these linkers will not have good volumetric capacity. It should be recognized that the increased surface area and gravimetric capacity is coming at the cost of volumetric capacity.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- Many collaborators are listed but coordination is not clear.
- There are excellent collaborators in quantity and quality, and the collaborations are meaningful additions to the results.
- Others are researchng MOFs, and its recommended to make the interaction among these groups more visble, if it does exist, since they are working on related topics.
- This project has an excellent set of collaborations.
- The collaboration with General Motors (GM) that led to the validation of PI's adsorption measurement is good. However, it was not clear what came out of the rest of the partners. Perhaps, the PI should consider limiting the number of collaborators at this stage of the project. Sometimes, having too many partners has its drawbacks.
- This project does involve a large amount of collaborators both within and outside of the HSCoE. It is also nice to see that the PI has initiated external validation of their results.

Question 5: Approach to and relevance of proposed future research

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

- The PI expressed a sequential problem-solving approach that dominated the strategy for the future work. Again, the problem requires parallel solutions for various issues. Most importantly is the ability to enhance the sorption energy, increasing the isotherm temperatures. Finally, the plan for doping the MOFs with coordinatively unsaturated metal centers is suitable.
- The future work target should be inline with the new DOE 2015 hydrogen storage targets.
- The 2010 third quarter go/no-go decision points are either well-defined or they appear to have already been met.
- The PI should prioritize incorporating active metals in the new or modified structures over increasing surface area.
- As stated, the next steps should focus on doping of unsaturated metal centers. However, it is not recommended that work continue to focus on the preparation of new MOFs with high surface area, because it is unclear how this will help achieve volumetric targets and/or increase binding. Surface area and gravimetric capacity are not the core challenges with this class of materials. Instead, efforts should focus on increasing volumetric capacity of their existing MOFs.

Strengths and weaknesses

Strengths

- This project shows a good initial proposal to explore the effect of open metal centers.
- The weight percent result is good.
- The project has a good approach.
- It seems to be scalable and recyclable.
- The synthetic capabilities are very good.
- The PI shows innovative approaches to synthesizing new MOFs with high-adsorptive surface areas.
- This project addresses critical factors of the hydrogen storage challenge.
- The project presented strong material synthesis and characterization capability.
- The team is very competent at preparing new linkers and MOFs and the rapid characterization of those materials.

Weaknesses

- The project is slow to reach its goals.
- Similar to other MOFs, the formation of compounds with high surface area was not an issue, and it seems that this is the target. Rather than creating MOFs with high surface area, it is better to focus on the available ones and try to apply the concept of open metal centers to determine how the heats of adsorption could be improved.
- None.
- The project may run into the familiar danger of past mistakes made by other adsorbent related projects. These are, specifically, being content with the temporary achievement of high-adsorption capacities in few materials at 77K, and losing sight of the ultimate target of ambient temperature operating conditions.
- There is too much emphasis on increasing surface area.
- The team seems to be too focused on preparing new materials with larger and larger linkers, yet it is not clear how this will help to get to volumetric targets.

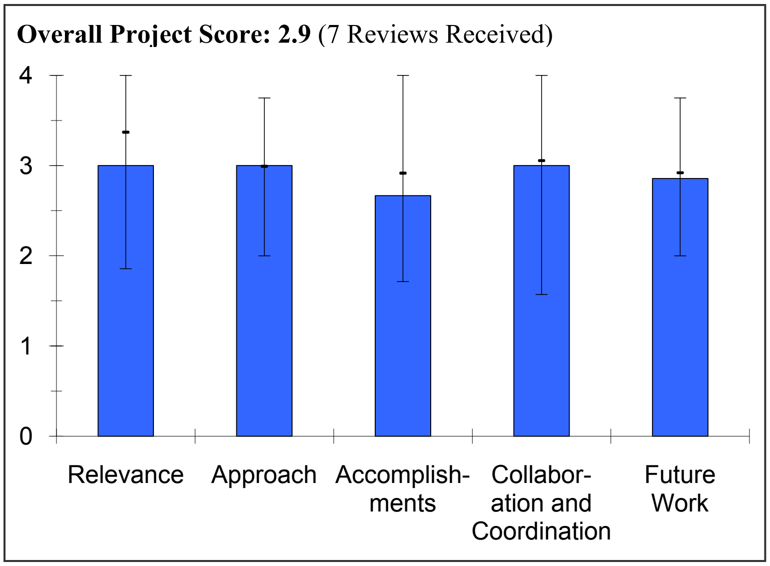
Specific recommendations and additions or deletions to the work scope

- The literature clearly shows that an extremely high surface area led to poor volumetric performance. It is suggested that the PI focus more on developing materials with the open metal sites, even with smaller surface areas, so they can at least measure the effect on hydrogen adsorption.
- The project team should look at the impact of compaction and of impurities.
- Guide materials selection on usable hydrogen (i.e. 2 bar is an empty tank), not total hydrogen.
- To keep the project, it is recommended that the project team devise a clear plan to achieve the targets that includes discovering a MOF with both high-surface area and high hydrogen affinity.
- Since hemoglobin contains iron, perhaps it might be used in the MOFs to increase the heat of adsorption. Other metals such as titanium might also be interesting.
- Aiming for high surface area should not be considered the project goal, but a means to reach a bigger goal.

- The data on additional physical and chemical properties – thermal and structural stability and sensitivity to air and moisture – would be helpful.
- The project team should also consider providing preliminary synthesis cost and scalability information.

Project # ST-19: Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

Peter Pfeifer; University of Missouri-Columbia



Brief Summary of Project

The overall objectives of this project are to: 1) fabricate high surface area, multiply surface-functionalized nanoporous carbon, from corncob and other precursors, for reversible H_2 storage; 2) characterize materials & demonstrate storage performance; and 3) optimize pore architecture and composition.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- This project at the University of Missouri-Columbia is another effort to develop high surface area and boron- doped carbon materials, mainly from natural resources, such as corncobs, for improved hydrogen storage via adsorption. The objective is to increase capacity and hydrogen-binding energies to facilitate great gravimetric and volumetric capacities at temperatures above approximately 100K. It is similar in scope and goals as most of the projects in the Hydrogen Sorption Center of Excellence (HSCoE) and other adsorption projects with the DOE/EERE Hydrogen Storage Program.
- The project is to synthesize high surface area carbon with surface functionality for superior H_2 storage capacity.
- The project is to manufacture monoliths for conformable, lightweight tanks.
- The design and test tank project is relevant to DOE storage goals. Increasing the hydrogen capacity beyond the the empirical relation, “Chahine estimate” of ~1 wt.% (percent by weight) capacity per 500 m^2/g surface area at 77K, if possible, would be an important contribution to reaching storage capacity goals.
- The project is aligned with major goals, though this could have been more clear in the presentation.
- The base material is free, which is excellent for project’s cost.
- The project’s objectives are well-aligned with the objectives of the HSCoE .

Question 2: Approach to performing the research and development

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

- The project is primarily an experimental study of production of carbons with and without supplemental addition of boron (B) additions. Some theoretical efforts to rationalize improvements by these approaches are included along with outside collaborations for characterizations via neutrons and other specialized facilities. A unique aspect of this effort is the use of neutron bombardment of boron-10 (^{10}B) nuclei to promote defect formation for the possible enhancement of hydrogen storage capacities. A reasonably systematic plan for variations in processing and boron-doping strategies is being followed to improve hydrogen storage properties.
- The overall approach is good. It tends to enhance the performance of activated carbon in a practical way.
- Approach is sensible in testing samples prepared with new techniques before moving on to more practical aspects such as forming compacts [monoliths]. External validation of hydrogen capacities of initial materials has proven to be an important aspect in the R&D approach.
- The material study is good so far, but multiple cycles and cycles against pressure are needed.
- It is not clear how much material can actually be processed in a reactor [facility for boron activation by neutrons], so this may result in inherently low volume production.
- This is a solid and reasonable approach of optimizing adsorbent surface area, structure, compost ion, fabrication, and characterization methods to achieve the desired hydrogen storage capacity and enthalpy goals.

- It is far from clear that materials processing via exposure to nuclear radiation is a feasible method for large-scale synthesis.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- Missouri has been able to demonstrate excess adsorption gravimetric capacities in the range of 4-7 wt.% (percent by weight) at about 77K, which is inline with similar results reported for other high surface area carbons. They have not yet achieved carbons with surface areas greater than 4,000 m^2/g as initially proposed. Missouri also had some success with their boron-doping procedures to give slightly higher binding energies (> 7 kJ/mole) at the initial stages of adsorption, which is also similar to the work of others. However, a pathway to significant adsorption at room temperature is not currently evident with these materials. The ^{10}B-neutron treatment apparently increases the capacity, but the mechanism is not currently identified.
- The progress is modest, and the enhancement of available materials is not clear. Moreover, there seems to be some contradictions in the results. For example, excess measurements on the "3K" sample show a similar behavior to "MSC-30", which is almost the same capacity with a maximum at around 40 bar, but a few slides later the same sample shows a higher capacity with no maximum and a higher binding energy.
- Also the rate of progress seems to be a little slow, only 30% completed since September 2008, and the remaining tasks will require much effort.
- Technical progress toward the project's goals has been good, especially with the cooperative validation of measurement and analysis of hydrogen storage capacities. More progress will have to be made to meet DOE targets. Neutron irradiation is providing interesting results but requires further analysis to understand the impact on hydrogen sorption.
- It was hard to appraise the actual progress.
- It is not too surprising that the neutron capture did not make the surface area grow, so it will be essential to get to etching experiments .
- They report a good adsorption level on a cheap material, but it needs to be confirmed outside [University of Missouri].
- The project found an increase in heat of adsorption from the addition of boron with a couple kJ/mole better binding.
- In light of the fact that the project is relatively new [DOE: the project was started late in FY 08] , the PIs have accomplished quite a lot on material synthesis, characterization, and modeling fronts.
- The project team has obtained a good agreement on the experimental and theoretical binding energy results on the B-doping.
- It is not clear that all of the data are reproducible.
- It would be very helpful if some of the higher performing samples could be sent to Southwest Research Institute (SwRI®) for independent measurements.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- Missouri has collaborated with National Renewable Energy Laboratory (NREL), National Institute of Standards and Technology (NIST), and other facilities to extend the characterization of their materials and independently validate the hydrogen adsorption capacities. They have also worked with outside theory groups. Closer interactions with the theoretical partners from the HSCoE could be useful.
- The collaboration is mainly on characterization and modeling. There is little to move the project ahead.
- Their collaborative validation with NREL is a positive step.
- Their collaborations are suitable and productive.
- The project team appears to have a strong collaborative partnership with NREL, Argonne National Laboratory (ANL) and NIST. However, it was not clear the specific roles of the international partners.

Question 5: Approach to and relevance of proposed future research

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

- It is not clear how future work is planned on room temperature materials.
- The work plan for the remainder of fiscal year 2010 and 2011 is reasonable. More characterization work to understand the role of neutron bombardment on apparent hydrogen-capacities should be included.
- Their work needs to proceed to the next phases of the project
- The future work is appropriate. The comparison of experimental and theoretical heats of adsorption is an important task.
- Etching is important.
- These are very good plans.
- The PIs should be encouraged to strive for reproducibility of their storage measurements.

Strengths and weaknesses

Strengths

- The systematic production and boron-doping of potentially inexpensive carbon adsorbents based on experimental work and theoretical support has been shown. Measurements and characterizations appear to be properly conducted.
- This is a good project with a practical approach for advancing the field.
- The project team appears to be able to functionalize materials through boron insertion.
- The use of low-cost material is a strength.
- While still conducting fundamental and mechanistic studies on the carbon materials, the project team appears to be guided by practical, real-world considerations. For instance, the project reports side-by-side adsorption results at 80K and 303K, which is very encouraging. A second example is the fact the PIs plan on monolith sorbent manufacturing and vessel test design. This is very positive and refreshing.
- There is potential for high uptake in relatively expensive materials.

Weaknesses

- The project has so far been unable to substantially increase either surface areas or boron-doping contents in these materials when compared to carbons from other sources. Improved methods to increase hydrogen-binding energies for larger hydrogen contents are needed if these materials are to have any application above cryogenic temperatures. There seem to be little cycling of the adsorption properties. This is especially important for the neutron-treated materials. This latter point needs to establish whether defects are created that can only bond hydrogen once and not provide enhanced capacities with cycling.
- The project is way behind schedule and needs more focus.
- It is not clear how much higher surface area materials will be achieved.
- There is a potentially high cost for processing.
- There is a high chance of hydrocarbon formation in nuclear-treated material.
- No outside confirmation was shown.
- Perhaps it is the presentation, but this work did not inspire confidence that the data were dependable.
- One of the three project objectives, namely optimization of pore architecture barely got a mention.
- It not clear that the favorable capacities of some samples have been correlated with specific material properties.

Specific recommendations and additions or deletions to the work scope

- The potential use of accelerators to enhanced etching may not be a practical step. Can the enhanced surface area process be achieved by other means?
- It is suggested that a greater effort be put into characterizing the presumed defects formed during neutron bombardment and the formation of new hydrogen-bonding centers.
- Desorption measurements of the doped materials is a must to check their reversibility. Results of the samples “3K” and “4K” need to be confirmed.

- It is recommended that further validation of experimental results be shown through collaborations, particularly on the measurements of isosteric heats of adsorption.
- The PIs need to have a credible third party to confirm the 7.2% result over a few cycles.
- The project team should look into the effect of lithium (Li) created from boron in nuclear-treated material, which may overshadow the boron effects or radiation tracks.
- This project should start addressing material pore structures and their effect on performance.

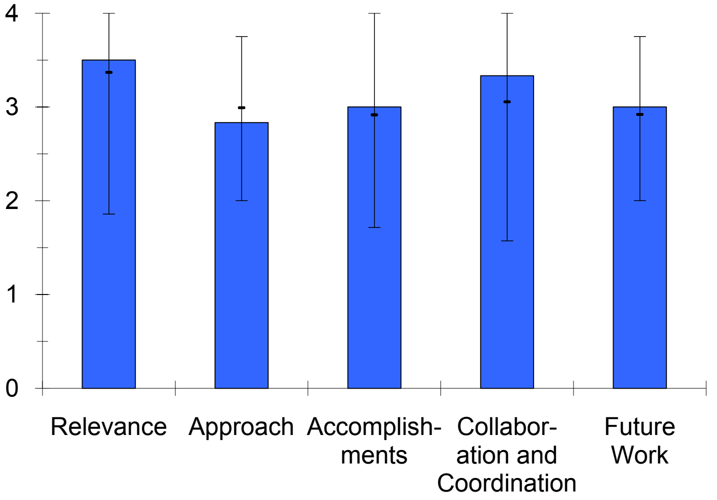
Project # ST-21: NREL Research as Part of the Hydrogen Sorption Center of Excellence

Lin Simpson, National Renewable Energy Laboratory

Brief Summary of Project

The National Renewable Energy Laboratory's (NREL) research in the Hydrogen Sorption Center of Excellence (HSCoE) is focused on key technical barriers in DOE's Hydrogen Program for on-board storage. NREL materials development focused on capacity, cost and kinetics targets, including 1) volumetric and gravimetric capacities; 2) optimize accessible specific surface area and pore size (e.g. decrease tank weight and size); 3) tune binding energies to increase capacities and control operating temperature; 4) improve kinetics for weak chemisorption, rate of hydrogen adsorption; and 5) develop next-gen sorption materials using inexpensive materials and processes.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- This project is focused on key goals, and the ones that truly drive the system.
- Their attention to costs up front is excellent.
- The project is well aligned with H_2 Program objectives and occupies a leadership role in the overall Hydrogen Sorption Center of Excellence (HSCoE) effort.
- There's no doubting that the HSCoE is a very relevant project.
- NREL's research is highly relevant to the overall DOE materials R&D effort. In particular, they are focused on addressing the key technical barriers associated with sorbent materials – volumetric capacity, optimization of surface area and pore volume, and enhanced binding. Additionally, to overcome these challenges, they are pursuing a wide range of novel materials including boron-doped carbon, spillover in carbons, and new zeolite-templated carbons.

Question 2: Approach to performing the research and development

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

- This center has had a remarkable turn around in its approach and outcome in the past five years. This is the best it has done. The approach is exactly what is needed to methodically develop storage materials.
- The materials being made are a good approach at this point in the program.
- The predictions are a good approach to guiding the more expensive and slower experiments.
- They [NREL] do serve a valuable role as coordinators as well.
- The Center relied too much on theoretical estimation to guide their materials research and was unable to validate these models based on the experimental results.
- For this late stage in the project, the technical approach is too broad and lacks specificity. The technical targets are firm, but the work should focus on a select group of materials instead of introducing new materials.
- Increased emphasis on optimization of hydrogen-binding energy is a good approach.
- The project milestones are weak and appear to be mixed up with deliverables. Publication or final reports are not milestones.

- NREL's approach to sorbent materials discovery is appropriately scoped and covers the primary challenges associated with that class of materials, which are volumetric capacity, binding energy, and spillover validation. NREL is also tasked with a great deal of the project management aspects of the overall Center at which they appear to be very competent, particularly in supplying measurement capabilities for CoE partners.
- It is clear NREL has been developing expertise in validation spillover in carbons. These efforts are applauded given the current lack of understanding and variation in results in the literature.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Specific-area based BC_3 adsorption is good. It is unclear if a higher area is possible but a good option. $LiBC_x$ was especially encouraging, and the PI should show a higher volume proof.
- A spillover capacity of 1% seems reasonable, although it is obviously not quite what is wanted but a believable result. Also, the much faster kinetics are perhaps due to shorter distance from the metal.
- For the BC_x systems, the results of higher uptakes for very low surface area materials needs to be explained. Otherwise, it is rather questionable.
- The analytical measurement capabilities and the “Best Practices” [measurement] document is valuable for future researchers in this area.
- The experimental results on the templated BC_x appear to be interesting.
- The PIs need to work on chemisorptive materials that are important to understanding the spillover mechanisms.
- The project team shows good work on improving the kinetics of spillover.
- A great deal of progress is evident for this project:
    - The characterization (X-ray photoelectron spectroscopy) and understanding of boron-doped carbon is at a high level and shows a great deal of promise. Further searches for materials that couple sp2 sites with high surface area are desirable.
    - The PI’s understanding of the synthetic challenges associated with spillover materials is showing progress. It was appreciated that both successful as well as unsuccessful results were shared, and it will be interesting going forward to understand why there are such mixed results for platinum (Pt) on carbons (e.g. validating the role of oxygen functionality).

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- This project has been very helpful to other groups along with deriving value from the collaborations.
- There seems to be a low level of collaboration. For instance, there were issues observed for spillover samples reproducibility when prepared by different groups within the Center.
- The project has extensive collaboration with its partners.
- It is very difficult to separate NREL's specific technical contribution outside the leadership role of the HSCoE.
- This project relies heavily on collaborations and is a true resource for other projects both within and outside of the Center with respect to measurement capabilities. NREL has continued to do an outstanding job of extending its knowledge and facilities to other groups. Additionally, as exemplified in their presentations, NREL has developed a great deal of individual interactions with other groups to pursue focused research.

Question 5: Approach to and relevance of proposed future research

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

- They are ready to wrap up this project. It is not clear that there is any more they could do.
- It is unsure what was meant by the fiscal year 2010 material development and Center go/no-go activities. There was no specific line for decision makers.
- The future work appears to be organized and focused on logical next steps considering the remaining time left in the project. Given that NREL has a good overall perspective of spillover materials based on interactions

within the Center and its one laboratory experience, it will be very useful to get their feedback in the final report with respect to the future potential for these materials.

Strengths and weaknesses

Strengths

- This project shows strong collaboration and has established access to other researchers and laboratories.
- The flexibility to fail fast and move on to new materials is a strength.
- The Center is finally starting to hit its stride. Unfortunately, this is occurring just as its funding is coming to an end.
- This is a very competent, highly collaborative research team.

Weaknesses

- The possibility to validate the theoretical estimates led the systems studied.
- There are almost no existing milestones or go/no-go decision points.
- Although an important future plan from last year's slide reads: "Provide materials/systems recommendations for DOE & Hydrogen Storage Engineering Center of Excellence", the project team did not come up with a recommendation of adsorbent materials inspite of specific requests. This is very troubling.
- The following comment from last year's reviewer remains valid: "The lack of a straightforward assessment of the severity and scope of the remaining technical barriers, as well as a statement concerning the extent to which the R&D in the remainder of the project will be able to effectively deal with those obstacles, are weaknesses."
- There is no follow up on the theoretical prediction of the calcium-decorated covalent-organic framework (COF) materials identified a year ago.

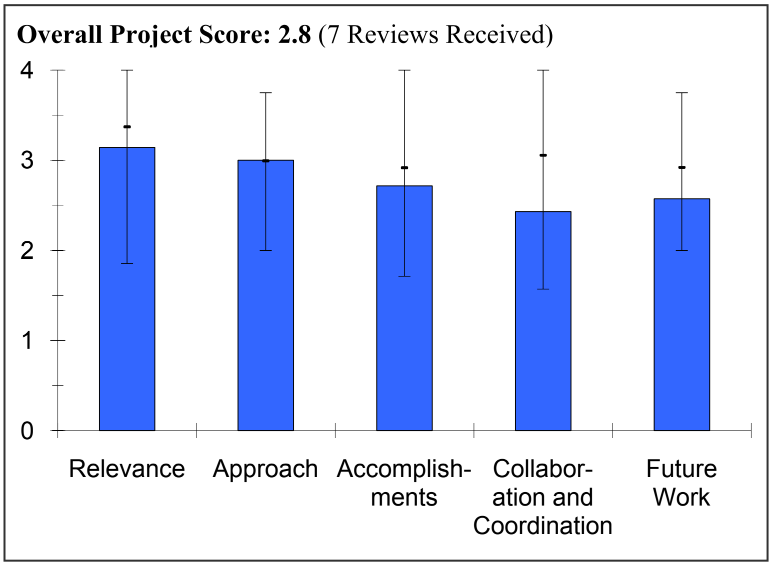
Specific recommendations and additions or deletions to the work scope

- It would be good to see more work on the reproducibility of spillover.
- The approach is exactly what is needed to methodically develop storage materials. This center has done an excellent turnaround in their scopes and methods during the past five years.
- This year’s presentation is probably one the best given during the entire project.
- The results are still far from the targets. However, the methodology and approach are perfectly suited for further material discovery, if the focus stays on developing room temperature, high-capacity sorbents.
- Among all the centers, this is the most promising area.
- The PI should keep refocusing on understanding the most promising materials systems.
- The final report should clearly contain specific recommendations of promising, downselected materials, or a class of materials, for future R&D.
- The experimental results on the templated BC_x should be verified by Southwest Research Institute (SwRI®) or other independent laboratories.
- Sorbents are an extremely important class of hydrogen storage materials.
- It is recommended that the DOE find a way to continue funding research in this area.

Project # ST-22: A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs for On-Board Vehicular Hydrogen Storage

Omar Yaghi; University of California, Los Angeles

Brief Summary of Project



The overall objective of this project is to achieve room temperature H_2 storage in covalent organic frameworks (COF) to meet DOE 2015 targets. The objectives for fiscal year 2009 are to: 1) conduct synergistic work between OmarYaghi (University of California, Los Angeles (UCLA)) and Goddard (California Institute of Technology (Caltech)), 2) build high-throughput preparation setups for COF synthesis using high temperature and pressure; 3) develop chemistry to realize stable frameworks, 4) introduce potential metal-binding sites through the COF synthesis, 5) determine atomistic connectivity of COFs using an ab initio charge-flipping method using powder X-ray diffraction data, and 6) predict adsorption enthalpy of H_2 on various metal sites.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.

- The project is designed to support the Hydrogen Storage Program and its goals and objectives.
- Overall, the work plan seeks to help the DOE meet the storage objectives by developing a methodology to synthesize new adsorbents.
- The synthesis and design of new materials is necessary for improving physisorbed hydrogen characteristics and allowing flexibility to develop higher-enthalpy-binding sites to allow higher-than-cryogenic temperature storage. The calculations are used to predict new materials and hydrogen-binding properties, but still there are barriers to synthesizing new materials owing to the complexity of the solvent-reactant energetics. The proposed combinatorial approach might yield fruit here, along with the condensation reactions to produce stable COFs.
- This project is very relevant. Metal-Organic Frameworks (MOFs) working at higher-than-cryogenic temperatures are definitely a huge plus.
- This program examines the development of boron- and nitrogen-doped COFs with the ultimate objective of adding metal sites for improved hydrogen binding. This objective is well within the scope of DOE objectives for hydrogen sorption materials.
- The project is in year 1 , is 20% complete, and has yielded one Journal of the American Chemical Society (JACS) publication, one Materials Research Society (MRS) Bulletin publication, and one Chemical Society Reviews publication.
- This project is critical to the Hydrogen Storage Program and fully supports DOE RD&D objectives.

Question 2: Approach to performing the research and development

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

- The approach is quite similar to that used in the past. It works from a chemistry standpoint but may need an adjustment to reflect the rather modest success with hydrogen storage in MOFs.
- The PIs did not clarify what special advantage is obtained with COFs as compared to what has been studied in previous work.

- The approach of increasing the delta-H and thereby achieve a higher isotherm temperature is not addressed adequately.
- There is still some work to be done to better integrate theoretical and experimental efforts; but to be fair, the project is still in an early stage (20% completed).
- The approach is close to being useful if a closer tie can be made between calculation and experimental validation and/or synthesis. The materials appear to be promising, but this can be said for the calculated properties of so many materials where the synthesis or realization of materials is unlikely. The incorporation of metal ions at sufficient densities and removal of ligands has proven to be an issue for many in this field. It detracts from the storage capacities in numerous ways from surface-area reduction and pore blocking.
- The approach based on modeling and high-throughput preparation is good.
- This researchers are taking a systematic approach to COF synthesis and X-ray characterization, while simultaneously seeking computational input for ideal COF structures and their theoretical hydrogenation properties.
- The systematic synthesis approach includes varying ligand types using a common imine chemistry.
- One impressive development is the use of a relatively new technique in powder X-ray diffraction analysis called charge flipping. Using this approach, the researchers were able to validate the synthesis of COFs comprised of five interpenetrating networks, which is a very complex structure.
- The approach needs to focus more on increasing strong binding sites for maximum hydrogen uptake capacity without losing pore volume.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- It's uncertain why COFs should offer any advantages over MOFs. This is an interesting, basic chemistry project with a very limited potential for practical hydrogen storage.
- Considering the resource allocation to this project, there was a higher expectation for technical progress.
- The project seems to be on track.
- Several areas have progressed in the synthesis areas: 1) high-throughput capabilities, 2) application of the well-known (in the field of crystallography) charge-flipping technique to poor quality X-ray data, and 3) condensation reactions to produce COFs. However, the progress is not without a cost and there is little material presented that addresses the hydrogen adsorption characteristics besides the values obtained form Goddard's calculations, which are prolific.
- Lots of COFs are synthesized, but there is not yet enhancement in binding energy. The PI needs to move to metal incorporation.
- The project is relatively new, and the researchers are off to a very strong start. The importance of systematically developing the COF-linker chemistry, followed by the COF synthesis and X-ray characterization, and then followed by the synthesis and characterization of metal attached COFs (which are recommended by theory before and after hydrogen uptake), is realized by the researchers.
- So far, at about 20% project completion, the COF synthesis, challenges toward X-ray characterization, and recommendations of computational collaborators have been addressed.
- The technical accomplishments to build high-throughput preparation setups and to develop a structural determination technique using the ab initio charge-flipping method seem on track. It is good to see the beginning of a modeling study for optimal-binding energy.
- The synthesis of new COFs through hydrazone condensation needs to be more focused for on-board vehicular hydrogen storage at room temperature.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.4** for technology transfer and collaboration.

- The project's collaboration is limited to just one partner, BASF. Surprisingly, no DOE or academic partners are involved.

- This project is not taking advantage of the rich environment and projects that have been funded and supported within the hydrogen storage program. This is a very critical issue, and if not addressed, it could have significant detrimental effect.
- The synthesis and calculation work seems to be pretty divided,and their work with collaborators toward the same general goal shows little interaction. There is no information on how BASF has been involved so far, though the collaborations from other MOF work is well known. But, given the early stages of materials synthesis and characterization, this may be expected.
- The PI's collaboration with BASF not really clear.
- The researchers are working closely with the Goddard group at CalTech with the idea that Yaghi's group will be able to synthesize challenging to prepare COFs predicted through Goddard's work.
- The project team's collaboration with other institutions are not clear.

Question 5: Approach to and relevance of proposed future research

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

- Their future work is hardly relevant to the end goal of designing novel, high-capacity hydrogen storage systems.
- While in the late stages of the hydrogen program, the proposed work here is reminiscent of the early part of the hydrogen project. It is not clear how the project addresses issues such as packing density and room-temperature operation.
- The project objective to integrate its theory and experiments is interesting and reflects a desire to address some criticisms of some projects that overemphasize the theoretical development and provide little experimental validation. The importance of studying some materials as proofs of concept that large storage densities could be achieved is understood. Some thoughts should be given to justifying or categorizing those materials in terms of the projected economic viability for transportation applications.
- There is not much provided, but there are logical progressions on material synthesis. It is crucial that the PI puts forth efforts to incorporate or partner with others, so that more characterizations can be performed.
- The proposed future research plan is only a restatement of initial objectives.
- Only one challenge that may arise was not addressed. That challenge is the understanding of neutron diffraction data after H_2 adsorption, given the difficulty in specifying the crystal structure determination of empty COFs.
- The project team's future planning is on track to employ metals to create strong binding sites, including a material design based on theoretical prediction. But, there needs to be more focus for on-board vehicular hydrogen storage at room temperature.

Strengths and weaknesses

Strengths

- This is a strong basic chemistry project.
- The project seeks to estimate the viability of a new class of materials for hydrogen storage.
- The project's way of integrating theory wtih experiments is interesting and reflects a desire to address some criticisms of some projects that overemphasize theoretical development and provide little experimental validation.
- The PIs exhibited good synthesis and materials development directions with some aid of computations.
- The group is excellent at synthesizing new compositions.
- The approach is very systematic and is inline with DOE objectives.
- The institution and the PI are well recognized in the area of this R&D.

Weaknesses

- The project has started to deviate its from original direction, which is designing novel materials for hydrogen storage.
- Although it is important to study some materials as proof-of-concept that large storage densities could be achieved, some thought should be given on justifying or categorizing those materials in terms of the projected economic viability for transportation applications.

- Mechanisms to dope the framework are sketched out, but the chemistry needs to be worked on. While the calculations presented as supplementary information give astoundingly high predictions, there is not much hope of them being validated experimentally. The calculations need validation from experiment and more hydrogen characterization needs to be performed to enable this.
- They need to focus on quantity instead of quality. The synergies between modeling and synthesis are not clear, and it looks like it is proceeding separately.
- The characterization tools seem limited to X-ray and neutron diffraction. Lots of information can be gleaned from fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) studies, particularly at the stage of H_2 uptake and assessment of its locale.
- Their approach is too diverse.

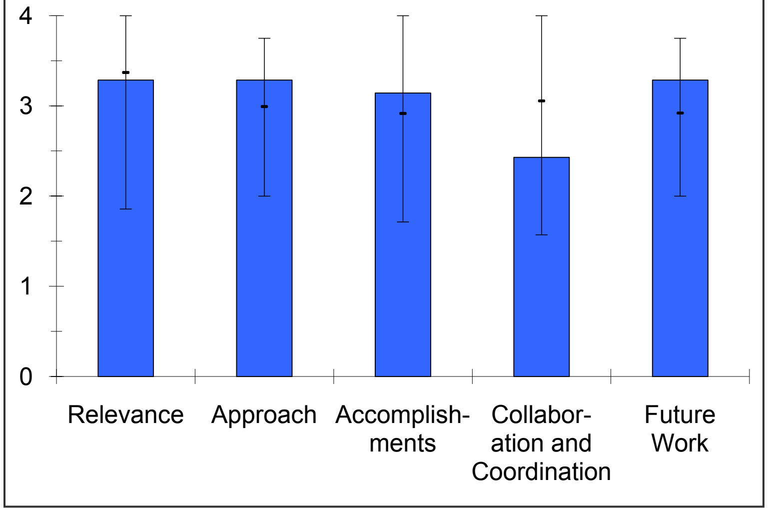
Specific recommendations and additions or deletions to the work scope

- It is recommended the DOE move the project to the Basic Energy Science.
- In view of the progress made in the past five years and the current trends in the carbon-based sorbent area, this program is out of synch. As a result, this project shows low relevance to the overall hydrogen program.
- It is recommended that the PI revisit the goals and objectives of this project. In view of shrinking resources without a significant change of scope and structure, it is difficult to rationalize the continuation of this project.
- It would be greatly beneficial if the group could synthesize at the least one composition already predicted by their own theory to have high-storage capacity at room temperature, instead of generating a lot of formula compounds. One example is metallated COF102-Li.
- The project team should consider using infrared and/or NMR as tools to assess H_2-adsorbed COFs the would determine the site locale of the H_2 relative to the COF structure.
- It is recommended that, should good candidates become available, large scale synthesis procedures be pursued.

Project # ST-23: New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

Randall Snurr; Northwestern University

Overall Project Score: 3.1 (7 Reviews Received)



Brief Summary of Project

The objectives of this project are to: 1) develop new materials to meet DOE volumetric and gravimetric targets for hydrogen storage, including metal-organic frameworks (MOF), polymer-organic frameworks (POF), and the tight integration of synthesis, characterization, and modeling, and 2) increase heats of adsorption as a means to meet volumetric and gravimetric targets at ambient conditions.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- The goal of improving gravimetric, volumetric and enthalpy of adsorption (delta-H) are aligned with program objectives.
- This approach is three-pronged with two synthesis efforts (MOF and POF) and theoretical prediction. The combination of MOF and calculation work is useful and is providing knowledge that can be applied towards the DOE goals, especially with higher enthalpy of adsorption sites controlled in MOFs. The POF work is likely to lead to the most scalable processing, but it currently suffers from low volumetrics, capacity, and enthalpy.
- It is not clear how this project addresses the gravimetric and volumetric storage targets. The PIs are clearly focused on increasing heat of adsorption, but the capacities are still extremely low. It seems very unlikely from the material presented that this work will lead to materials that meet the 2015 targets.
- This project is relevant to the DOE's goals of increasing the temperature of physorption materials while maintaining practical hydrogen storage capacity.
- It is necessary to discover and develop new materials to be able to meet the DOE targets and the Northwestern group is combining theory, synthesis, and characterization applied to new concepts and new materials.
- This project is highly relevant toward achieving DOE hydrogen storage programmatic goals, specifically focusing on gravimetric and volumetric capacity and heats of adsorption in sorbent materials, MOFs and POFs, through experimentation and modeling. The concept of using strong-binding linkers and/or introducing metal ions and atoms is not completely novel, but nevertheless should provide a fruitful modeling and/or experimental space.

Question 2: Approach to performing the research and development

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

- This project has just started. [DOE: The project started in late FY2008.] The problems the PIs will face will come from the approach of using high-charge-state linkers (that are desired for the end-product) to attract molecular hydrogen, with the nature of these charge states in order to synthesize the materials in the first place. This is probably reflected in the lower-than-theoretical surface area that the synthesis has yielded to date. It is possible that remnant liquid from the processing will be retained within the structure and be difficult to remove. Moreover, while the charge states of the linkers may serve to improve the sorption at the charge site, subsequent hydrogen will invariably have sorption enthalpies that are smaller. While a MOF with a high average of sorption enthalpy as a function of loading is desirable, this will probably be too difficult to achieve. It is good that the PI recognizes this though.

- There is strong relationship among the PIs, and the separation of issues leads to a well-rounded approach with more focus on the MOF work than POFs. This is likely because of the ease of calculation of periodic MOFs compared to the short-range-ordered POFs. More emphasis on the latter would be useful.
- The modeling seems to work well. It is very useful to predict isotherms, heats, and diffusivities.
- The investigators have done a good job predicting materials with higher heats of adsorption and following through with the experimental work to prepare and test the materials.
- However, it is not clear how this project will ever meet DOE gravimetric and volumetric targets, even given the most optimistic results.
- More collaboration within DOE program would be beneficial. Good collaboration between synthesis and modeling and more hydrogen storage characterization is needed.
- There are potentially strong linkages between theory and experimentation.
- The combined experimental-modeling approach for materials discovery and optimization is probably the biggest strength of this project. In particular, the modeling activities have proven instructive for the up-selection of promising linker-incorporated metal ions (alkoxides) for experimentalists to focus on. Simultaneously, experimentalists have been productively synthesizing high surface area POFs and MOFs and testing their hydrogen binding and adsorption properties.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- The theory and empirical components of this effort appear to work well together, and they have produced a few ideas and results of potential interest.
- The synthesis and validation that delta H can be increased uncontrollably in these MOF materials is an achievement along with the novel zwitterionic systems. The increase in delta H in these systems is presumably from the charge seperation in the framework, but the narrow pore size could also contribute to the high delta H. It would be worthwhile trying to separate these factors, perhaps with calculations.
- For the POFs, the moderate surface areas give rise to a rather low 77K hydrogen adsorption capacity of 1.4 wt.% (percent by weight). The expected maximum excess adsorption would be more like 3 wt.%, yet the available data does allow this determination. Pore size distributions would be helpful to use in interpreting the delta H values since they seem rather narrow.
- The calculations seem robust compared to the literature and experiments. The highlight might be that magnesium (Mg) is a good receptor.
- The project presented nice accomplishments. It has met milestones for heat of adsorption and surface area. However, even while meeting both targets, the H_2 uptake is still very low, approximately 1%, even at 77K. Is there any hope that this approach will ever meet DOE targets?
- Modeling efforts are making progress and pointing to new Mg-alkoxide MOFs with better H_2 storage properties, but these need to be validated through the synthesis of the materials. The PIs have achieved at least two new MOFs and three new POFs. However, all have relatively low surface areas. Novel synthesis routes are promising, but the progress on synthesizing new materials could be better.
- The Northwestern group has synthesized several new MOFs and POFs and achieved the current year's target of improving the heat of adsorption. The new concept of introducing cations is very interesting and seems promising.
- The project team's progress has been somewhat modest so far, but the work is of high quality and this is still a relatively new project.
- Clear progress has been demonstrated on the synthesis of unique zwitterionic MOFs and POFs achieving their 2010 enthalpy milestones (i.e. 10 kJ/mol). These materials appear to be distinguished, in approach and composition, from the many other related MOF projects. For the modeling work, the impact of catenation on binding, and likely volumetric capacity, is very interesting. The alkoxide aromatic predictions are interesting; hopefully, this work can be experimentally demonstrated despite the lack of current successes of lithium (Li) introduction into MOF linkers. The further linking of experimental and modeling efforts is encouraged.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.4** for technology transfer and collaboration.

- Collaboration with the PIs appears good. Partners and collaborations have not been featured in the past year, partly because this is a fairly new project. The lack of materials characterization would warrant they expand their collaborations to get high-pressure isotherms, plus some characterizations from their long-term collaborators.
- There is good collaboration within the group, but no collaborations with DOE H_2 program were shown. Collaborations with other laboratories are getting started. It would be beneficial for the PIs to collaborate more closely with the Sorption Center.
- It is very important to maintain good collaborations with experimental groups to prepare and test predicted materials.
- Collaborations with experts within the program should be increased, particularly with respect to hydrogen storage measurements.
- No formal collaborations exist, but they are utilizing other groups' expertise. There does not seem to be a need to include any other researchers at this stage of the project, but they are likely to do so in the near future.
- There is nothing of significance related to H_2 storage at this point beyond Northwestern. However, the team at Northwestern is already well rounded.
- Given this is a relatively new project, it is understood that some time is required to develop external collaborations, especially since the Sorption Center is ending. It does appear they are beginning to leverage characterization resources at Argonne National Laboratory (ANL) and Universidade Federal Ceara, (Brazil). This project does rely on extensive internal collaborations involving multiple professors at Northwestern. Additional future collaborations with other researchers like Hong-Cai (Joe) Zhou at Texas A&M University might also be logical.

Question 5: Approach to and relevance of proposed future research

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

- The plans make sense on the basis of the initial proposed work. The problem with the project from a programmatic standpoint is the goal of a high heat of adsorption.
- Capitalizing on the recent results, the direction forward seems well judged, specifically placing more emphasis on the full adsorption range to compare deliverable hydrogen capacities to the 2 bar low pressure limit for fuel cells.
- The project team's future work looks good.
- The proposed future research is inline with the recommendations for speeding up synthesis, characterization, and validation.
- Their theory predicted the introduction of Mg to be beneficial for increasing H_2-content (wt%), and it will be interesting to learn from the next year's experiments if the synthesized compounds meet the expectations.
- The future work seems to be a logical extension of current progress. In particular, it is recommended and listed that the cation incorporation into the MOFs remain a primary focus. This work supports the theoretical predictions and should help to augment hydrogen binding strength. The expansion of modeling efforts to include POFs should also remain a priority to strengthen linkages to experimentalists.

Strengths and weaknesses

Strengths

- There is good collaboration and recognition on the part of the PIs in regards to the goals they can achieve that are within reason.
- The combination of the three PIs and their expertise areas is a strength.
- The project team presented very nice modeling and experimental work. The project is well organized, and investigators work well together.
- The systematic studies are showing steady progress.
- There is a wide range of synthesis capabilities. POFs offer new and potentially tunable material for H_2 storage.

- The Northwestern group is introducing a new concept for materials discovery and for improving existing materials. The approach is solid.
- This is a highly organized, focused, and efficient team. They are showing great progress!

Weaknesses

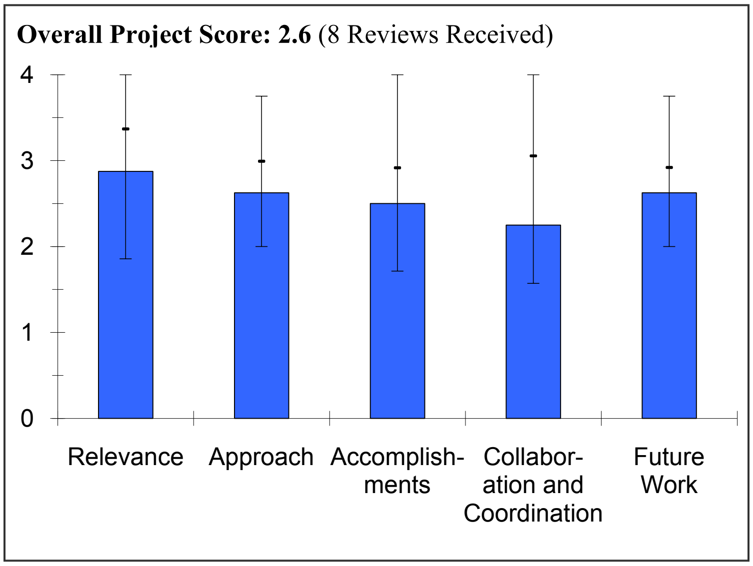
- A single value for a high heat of adsorption will not address the technological issues. If an initially high value for the isosteric heat decays as a function of loading, then the isotherm behavior will be such that a substantial fraction of hydrogen is retained within the material at the greater than 3 bar pressures that is required for fuel cell delivery.
- They lack the inclusion of practical systems considerations.
- A primary weakness is that there is no clear indication of how they plan to significantly increase the capacity to meet the targets. They need to clearly show what materials properties (i.e., surface area or heat of adsorption) are necessary to achieve the targets.
- This is a very nice basic science project, but it is not well suited for an applied program.

Specific recommendations and additions or deletions to the work scope

- The project is still relatively new, but they should try to create more overlap in scope and search-space between modeling and experimental efforts.
- The project team needs to have fuller characterization.
- More direct partnering with other DOE projects to validate measurements is needed.
- High-pressure measurements are needed to demonstrate maximum excess capacity of these materials.
- Experiments of full isotherms to high pressure should be performed on current materials.
- In a later phase of the project, a task for validating the experimental results should be added on.

Project # ST-24: Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

Angela Lueking, Penn StateUniversity



Brief Summary of Project

The overarching objective is to synthesize designer microporous (d < 2nm) metal-organic frameworks (MOF) with catalysts to enable hydrogen-spillover for H_2 storage at 300K-400K and under moderate pressures. The objectives for the past year have been to: 1) synthesize eight microporous metal-organic framework (MMOF) structures with variations in surface chemistry, pore diameter, pore structure, and surface area measurements, 2) adapt volumetric measurements to enable rapid screening tests (RST) at high pressure towards a go/no-go decision point, 3) validate RSTs against published activated carbon and spillover materials at P<80 bar and 298K, 4) conduct an initial screening via RST secondary spillover tests that shows 2.4 wt% (excess) achieved at 300K and 80 bar relative to a 1.5 wt% benchmark, 5) demonstrate the importance of preparation conditions on uptake with a three-fold enhancement in published literature with proper activation, and 6) explore methods for pressure-induced hydrogen gas trapping.

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.9** for its relevance to DOE objectives.

- Spillover is a controversial methodology that has mixed results from different laboratories, and here $2 million is being invested to shed light on this subject.
- It seems that the project primarily should focus on spillover and improve the lack of knowledge in this area while validating the high value results in the literature.
- Most of the project's aspects align well, especially the 5.5% go/no-go point projected in fiscal year 2011.
- The investigators are adressing key barriers to H_2 storage. The focus on room temperature adsorption is good and appropriate for this project.
- It is unclear how the H_2 trapping work will really be beneficial. Even if a perfect material is found, it is difficult to see how the logistics of charging at high pressure and storing at low pressure will work. Either the onboard tank is built for high pressure where there is no need to store at low pressure, or it performs offboard charging, which is much less attractive.
- The development of new materials is relevant to the program.
- It is not clearly stated, but it is presumed that this project has a focus to improve mass and volume percent.
- It would be desirable to obtain a high-capacity material that operates at room temperature, and the Penn State group is utilizing MMOFs to reach this goal, which is aligned with the needs of the Hydrogen Storage Program.
- A study of the importance of the hydrogen receptor in spillover is of great importance.
- The objectives of this project, concerning the synthesis of spillover MOF materials, aligns well with DOE R&D goals. Given that perhaps the most critical challenge associated with MOFs is their relatively weak binding of hydrogen that leads to cryogenic operation, this project's objectives are very relevant.

Question 2: Approach to performing the research and development

This project was rated **2.6** on its approach.

- The approach of independent synthesis and validation of spillover results is valuable, and this project is well designed to do so. The experimental and preparation methodologies are in place to make significant progress in the near term. The synthesis of new MOF is of moderate value here but is a little premature given the uncertainties in the spillover process itself. The other aspects of the project are academically interesting but have little chance of achieving DOE goals given the small amounts 'trapped' at cryogenic temperatures. Their approach for MOF work is good but could be more systematic. It would be useful to establish correlations between various functional groups and H_2 uptake and not just focus on capacity.
- What is the role of spillover? How are these materials different than other MMOFs with functional groups? Is the metal just acting as a disassociation catalyst?
- On slide 12, investigators state that "extrapolation suggests greater than 4% at 100 bar". Is it fair to talk about extrapolation here? Don't all of these systems saturate at some surface coverage?
- The main goal of the project is to produce catalyzed MOFs for hydrogen uptake by spillover. Beyond this, the R&D approach to meeting DOE storage goals are not particularly clear.
- The PIs include engineering effects that are good.
- Trying to gain understanding of what factors matter is good, but it is not clear that the specific approach will allow predictive power but only show some generalizations.
- Looking to maximize dispersion; attempt to lower pressure is needed.
- Pressure quenching is of questionable value. The cartridges are not a very likely route.
- To improve the hydrogen adsorption by a spillover mechanism, the Penn State group is designing materials by introducing functional groups. This is a promising approach. However, the second approach for the materials design seems less promising. The H-trapping via hysteretic sorption provides a way to explore the rigidity and flexibility of structural frameworks for trapping hydrogen, but it is questionable how this can improve the gravimetrics.
- While it is good to have a wide-ranging study, casting too wide of a net can lead to confusion rather than clarity. It is recommended that the PIs consider conducting a design of experiments to isolate the importance of, or establish trends across, a few key materials properties by looking at only a subset of possible receptors.
- A nice example of this type of approach was presented in their work already, according to the slides on the importance of preparation conditions.
- The overall approach of pursuing spillover MOFs that surpass current state-of-the-art isoreticular metal organic framework (e.g, IRMOF8) is appropriate for down- and up-selection of materials. It is unclear what the specific rationale is for MOF selection that could be more developed. However, there was good detail pertaining to the approach for maximizing metal dispersion. The screening approach involving a single point isotherm at approximately 80 bar is very useful and efficient, especially given the often slow kinetics for this material class. It is very ambitious to pursue 5.5 wt.% within the second year of the project, which could be slightly softened.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.5** based on accomplishments.

- Several systems have been measured, and literature results seem to be validated. From the synthesis of already-known MOF systems, their preparation for spillover studies has produced some respectable achievements, and the academic aspects of the thermodynamic trapping studies show promise.
- Overall, the results are inline with expectations of material properties and correlate with the best there is in terms of spillover.
- While the quick, one-step throughput has led to efficient down select criteria, the lack of desorption data or evaluation of possible side reactions is a major deficiency. It is apparent in the 2.5 wt.% sample reported the rapid uptake was a completely different mechanism from the other samples. This is usually because of side reactions. The changes in the X-ray diffraction (XRD) data needs to be better controlled and/or explained. The PIs need the full kinetic evaluation of any and all transients.
- What type of temperature regulation is on the high-pressure volumetric system?
- The researchers need to quench after each single dose, pump out headspace, and evaluate the possible by-products on a Temperature Programmed Desorption (TPD) system.
- What is the expected surface residence time of any hydrogen?
- The PIs need some cryogenic (77K) data to establish the side reactions versus physisorption.

- The idea of ball milling or grinding the MOF is not desirable. During synthesis, it is suggested that the different conditions to vary nucleation and growth parameters to get different particle sizes.
- The project team should also report approximate volumetric data.
- It was not clear whether there were any plans for using a bridging material. The investigators synthesized a number of MOFs with various functional groups. Only one sample, on oxygen-functional group modified MOF (MMOF=O), shows promising capacity, but they need to demonstrate reversibility. The XRD clearly indicates that a structural change takes place, so it is not obvious that a second uptake will be the same as the first. Without a second H_2 uptake curve, we can not really be sure. Either way, it does not look like the group will meet 2011 go/no-go of 5 wt.%.
- Seven or eight MOFs were synthesized. Single point hydrogen absorption data measurements were collected on six of these. The benchmark data are far from the DOE goals. The validation of reversible hydrogen storage was not performed.
- The project shows decent progress. The project team made a series of MOFs with different functionality pore size.
- The PIs are looking at a variation in synthesis conditions.
- In reference to 2.4 wt.% at 80 bar in oxygen double bond material, the kinetics are slow and the results about desorption are not yet known.
- This seems to be a very challenging project, but they got results pointing toward the right direction by introducing oxygen as a functional group. This approach increases the hydrogen uptake to 2.4 wt.%, which is still quite modest and slightly higher than for interstitial metal hydrides. What information is there about cycle life?
- While the project is less than a year old, it is expected that progress will pick up in the second year.
- A great deal of technical progress has been made with respect to the rapid synthesis and property screening of spillover MOF materials. At the outset, it was good to see a validation of results from the literature. The primary focus of this year appeared to be on evaluating (approximately 8) MOFs possessing diverse surface chemistry, pore diameter, and structures. Based on the final uptake data, some structure-property trends were identified. What was not analyzed yet was the impact of processing, such as ball milling, on the MOF materials themselves. What is the impact of processing on the structure of the materials? This suggested investigation is already listed in the future work, which is a great next step. The idea and practical benefits of trapping are not yet clearly understood. The PIs might consider deemphasizing this work unless practicality is demonstrated.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.3** for technology transfer and collaboration.

- The MOF synthesis and spillover work is naturally well tied but removed from the theoretical input by Milton Cole. Cole does, however, tie in with the synthesis of flexible MOFs and calculations of the thermodynamic functions. There is no evidence of further collaborations other than these three aside from what is planned in the future.
- The project team needs to set up a collaboration for independent validation of data and/or look at downselected materials for multi-step, high-pressure systems. They should consider National Renewable Energy Laboratory (NREL), Southwest Research Institute (SwRI®) and/or National Institute of Standards and Technology (NIST) would be possible options. Validation is very important to reach the 5.5 wt.% point to determine go/no-go.
- It is unsure with whom they are collaborating. It looks like all collaborations are pending or ongoing discussions. The project could benefit from collaborating much more with the sorption community.
- Their collaboration activities are mostly focused on modeling. Validation through collaborations with other laboratories is highly recommended.
- The project's number of collaborators is low, but the team is planning more.
- There are some collaborations ongoing with future plans to increase the network.
- This project relies on collaborations among three institutions, although the specific roles of these partners were not given in great detail. Additionally, with respect to collaborations outside of this project, it appears that some are being developed, for modeling for instance, which should benefit this project. This project is still relatively new, so some understanding is given to the time it takes to develop these collaborations.

Question 5: Approach to and relevance of proposed future research

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

- There is continuity in the future plans, but the focus on the DOE goals needs to be more concentrated. Spillover should be the emphasis, while the other aspects are reduced in priority. Given the description of how sample conditioning affects spillover, there is a great need to examine this along with the factors affecting kinetic uptakes.
- Apparatus modification that will allow for desorption studies are also necessary and needs to be addressed in the near term.
- There is no clear roadmap to meeting the targets in the future work plan.
- A more systematic study is necessary to incorporate predictions, materials design and synthesis, characterization, and feedback to modeling. This approach would require more effective use of collaborations.
- Getting validation of the measurement techniques through a collaboration with NIST is an important step.
- The future work appears to be relevant to the project's goals, but the outlined approach is vague.
- This project is good but needs the benefit of outside collaboration with experts in MOFs.
- The future work presents a great extension of the current results. In particular, the investigation and impact mixing methods and surface chemistry should be very instructive for further definition of structure-property relationships. The suggested future work involving modeling and/or techniques would be additionally valuable, where spillover could be characterized *in situ*. The PIs should deemphasize their work on trapping unless practicality can be demonstrated and understood.

Strengths and weaknesses

Strengths

- The individual capabilities of the PIs bring a lot to the project, but it needs to be focused in one direction. The approach to validate spillover is important, and attention needs to be placed on understanding the processes involved.
- The insight of the PI and the ability to make a range of materials for evaluation is a strength.
- The project team has done nice work on the synthesis of MOFs with different ligands and functional groups.
- The team's engineering aspects in trying to get at the mechanisms and important parameters is considered a strength.
- They are a very capable team who are making great progress, especially with the synthesis and characterization of spillover MOF materials.

Weaknesses

- The diversity of interest of the three PIs is pulling the research in three different directions and unequally at that.
- There is a lack of multi-cycle data and in any evaluation of side-reactions in the current data set presented.
- The project will not likely meet its go/no-go point since only one sample shows a capacity greater than the benchmark. There is no clear path identified for meeting targets.
- The project is lacking significant validation of results through cycling and collaborative validation measurements.
- The team showed little understanding of MOFs.
- It is not clear how a higher-gravimetric capacity will be obtained. The project has a go/no-go decision in the third quarter of the second year on reaching more than 5.5 wt.% at 300K-400K. If this is not achievable, this approach may be too challenging for the project to continue.

Specific recommendations and additions or deletions to the work scope

- They need a design of experiments, not just variation in the parameters.
- There should be more efforts in determining the controlling factors for spillover and additional work on identifying the barriers to improving the uptake and desorption kinetics.

- The PIs should focus on spillover on known materials and their characterization. They should reduce their other efforts at this point in time, especially since the 77K and 87K uptakes are so low that there is little hope of pressure and temperature swings reaching DOE goals.
- The PI needs to set up a collaboration to validate absorption data and assist with the adsorption and desorption evaluation of the materials used for a faster downselect process.
- A more systematic study of how various functional groups affect storage capacity would be useful. If a high capacity material is not found in this effort, they may be able to learn something (e.g. empirical trends) that could be applied to future work.
- It is not certain that the trapping work is appropriate for an applied program. The science is interesting, but it's not clear how this type of material would work in a real system.
- Validation of results should include H_2 sorption measurements on blank samples under the same conditions as spillover and hysteretic adsorption results. The materials should be cycled to confirm reversible hydrogen storage and not simply hydrogen uptake through other reactions.
- The project team needs to gain a deeper understanding of MOFs, perhaps by entering the research community who focus on MOFs and collaborating with more of them.
- It is recommended that less, or no, emphasis be spent on the approach with H-trapping, and instead focus on the addition of functional groups on the MMOFs and the other tasks they listed in their future work slide. It is also recommended to add on a task for durability (cycle life) of the upselected materials.

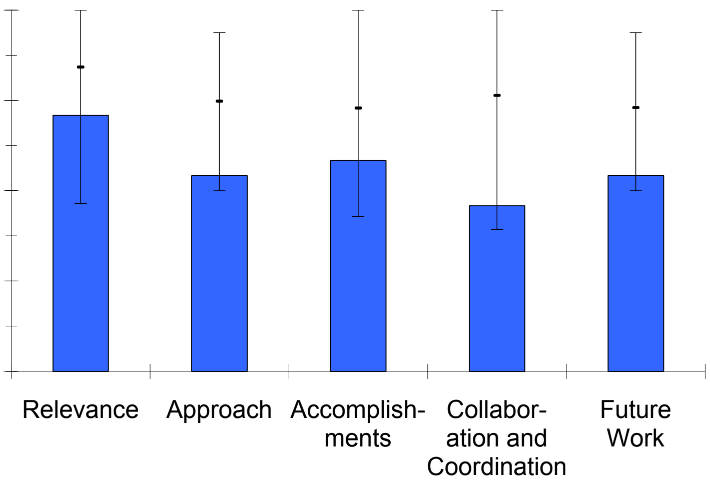
Project # ST-25: Polymer-Based Activated Carbon Nanostructures for H_2 Storage

Israel Cabasso; State University of New York-esf at Syracuse

Brief Summary of Project

The overall objective of this project is to develop and demonstrate reversible nanostructured polymer-based carbon on hydrogen storage materials with materials-based volumetric capacity of 50 g H_2/L, with potential to meet DOE 2010 system-level targets. Tasks are to: 1) perform precursors processing, including material development, modification and characterization; 2) perform nanostructured carbon preparation, including high surface area activated polymer-based carbon, analysis morphology, and production scale up; 3) investigate hydrogen storage, including physisorption and chemisorptions; and 4) perform hydrogen storage testing.

Overall Project Score: 2.3 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.8** for its relevance to DOE objectives.

- The synthesis of microporous carbons is of relevance to the program, as it addresses the problem of volumetric storage in materials of this type.
- This project successfully develops high surface area polymer-based carbon which, with an appropriate doping, will combine physisorption and chemisorption of hydrogen with an improved hydrogen binding energy. The material processing can be scaledup, inexpensive, and approach some of the DOE targets.
- Nice focus on materials exhibiting a combination of high gravimetric storage capacity and durability (cycle life).
- The overall value of investigating inexpensive adsorbent materials is relevant and supports the DOE RD&D objectives. The explanation of the path to the target through improved surface area or pore size provided a good vision of the project focus.
- The program is focused on development of high surface area polymer-based carbons. The PI showed reasonable storage at cryogenic temperatures. However, some of the positive results are somewhat surprising, and the PI made no attempts to explain these results even when asked.

Question 2: Approach to performing the research and development

This project was rated **2.2** on its approach.

- The approach of the PI makes sense, but aspects of the work defy any rationale in motivating the need for the assessment of the materials that have been synthesized. For example, the reason for the addition of lead zirconate titanate (PZT) was done without any strategic explanation given. While some important empirical discoveries have been achieved accidentally, many things are unclear, such as:how the PZT was incorporated; the difference in surface area after incorporation; the amount of PZT added and whether the addition of this PZT was used as part of the weight percentage (wt%) normalization of the gravimetric uptake.
- The approach to make the carbon material is good; however, it requires better understanding of its morphology; e.g., connectivity of the pores.
- It is not clear why investigators doped with PZT.
- It was not clear what they are trying to do with the Monte Carlo calculations. Slide 16 suggests titanium and magnesium open up the structure, but it doesn't look like there has been any attempt to make this material.

- The project approach was unclear. It was difficult to gain confidence in the results since the approach needed further definition. During the AMR presentation, it was explained that the best results were from material that was 4 years old, but this information was not linked to the project approach or other materials. The volumetric capacity calculation needed further development and explanation to gain confidence in the values presented.
- The results seem to show that the PI has fairly good control over the morphology and chemistry of the carbons created.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.3** based on accomplishments.

- No measurements of carbon that the reviewer is aware of have ever shown excess sorption values of over 6 wt%. Data as measured by the Gas Technology Institute (GTI) appears to show 7 wt% uptake at around 50 bar pressure. This is an astonishing value for a pure carbon. Unfortunately, slide 11 shows a collection of data from different laboratories on different materials, so it is difficult to assess the utility or accuracy of these results. The only data the reviewer does trust are those from Quebec, showing the expected 5.5 wt% uptake seen in most carbons. Data from Hiden systems could be inaccurate.
- The plot on slide 19 is a misrepresentation of the uptake as it is data taken at one bar pressure. What this data actually show is the enhancement of adsorption enthalpy at low pressure. The PI cannot extrapolate data taken at one bar to determine the overall uptake of a material. While the initial slope of the isotherm with enhanced enthalpy will be sharper, the ultimate uptake at the surface excess maximum invariably depends on the surface area.
- In slide 12, the PI notes a 46 g/L volumetric density, but this is a deceptive number, the derivation of which has not been explained. The implication is that this is the density that might be achieved by using this material in a tank. What the PI has omitted is the fraction of bulk density by which this material can be compressed. After that, a gas law contribution needs to be worked out for the rest of the tank volume. PIs should not be allowed to present a volumetric density unless this analysis has been worked to completion and an actual fraction of material bulk density is presented.
- The progress was made in testing and in reproducibility of production. Very good numbers were obtained for gravimetric capacity at 77K. Progress in theoretical simulation gives some indication on prospects of having higher temperatures adsorption using transition metals.
- Very large volumetric values—hard to believe for uncompressed powders.
- Results show very high capacities, but for samples that were 4 years old. It's not clear what new materials development work has been going on for the past four years, whether the new materials show lower capacities, or whether there were no new materials developed over the past four years.
- All of the diatomic hydrogen uptake testing was done by collaborators. It is not at all clear what the investigators actually did with their funding.
- The major accomplishment is that at 77K, some of the materials investigated here show high surface area and up to 7 wt% materials hydrogen content, which is close to meet the DOE system gravimetric target, however the materials' capacity must exceed the system target. Kinetics is, however, not evaluated, or perhaps not reported here.
- The concept of introducing a carbon alloy is interesting and the simulations show promise; however, the preliminary experimental results only show a lower gravimetric capacity and it's unclear how they will proceed from here.
- It was difficult to assess the accomplishments of this project since the presentation needed further explanations of the items in the project summary. The comparison of excess gravimetric hydrogen uptake isotherms from various sources was a useful assessment.
- The volumetric capacities look (surprisingly) good?! There needs to be an explanation for this high capacity in such a low-density, high-surface area material. The PIs acknowledged that they did not measure these capacities directly, but rather inferred from density. Given that these numbers are so surprisingly large, a direct measurement would be necessary (or at least welcome).

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **1.8** for technology transfer and collaboration.

- The extent to which collaborations are noted in the presentation are only relevant as they indicate measurements performed at other laboratories. The nature of any real interaction that may have occurred is not clear.
- There was increased collaboration, especially in the area of testing and establishing independent measurements.
- There are no clear collaborations within the DOE Hydrogen Program. Investigators are working with a United Kingdom (UK) group for uptake measurements. The project would benefit from more collaborations with other sorption groups within the DOE program.
- The collaborations listed seem to be for validation of results and for obtaining precursors, but there doesn't seem to be any scientific exchange or discussion with other research groups.
- The collaboration partners seem to be limited and could be improved.
- The previous reviewers suggested that this project should have collaboration (or at least some contact or communication) with others who are working with polyetheretherketones (PEEK). It appears as though the PI is not familiar with other similar efforts in the field.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.2** for proposed future work.

- The PI apparently does not recognize that some enhancement of sorption enthalpy of the melem-based material has already occurred. Not having presented an actual value, the rest of the goals of their research, while sensible in principle, leaves the reviewer to wonder what approach the PI will take in addressing these values. In addition, it is not only the initial enthalpy value that needs to be addressed, but the range of isosteric heat over the sorption range (as other PIs have presented). There is, potentially, great interest in materials of this type. The execution of this work in determining the thermodynamic quantities of interest, given the present list of collaborators and the questionable high pressure data that has been produced so far, represents a huge disappointment, given where this research could go.
- The proposed future work in improving the binding of hydrogen is not very clear. It is also not clear if, with the methodology of the project, future improvements of pore/surface area parameters can be achieved.
- The future work plan is appropriate.
- It would be useful to measure sorption enthalpies (ΔH) for these materials.
- It would be interesting to learn the strategy for obtaining adsorption at elevated temperatures of the PEEK materials.
- The next steps appear to be headed in a correct overall direction, but it is unclear if any of these items can provide enough improvement to achieve the acceptable binding energy. An assessment of the potential for improvement would be useful in the future work plan.

Strengths and weaknesses

Strengths

- Sorbent materials are of interest and show some interesting thermodynamic data.
- This project successfully develops high surface area polymer-based carbon, which, with an appropriate doping, will combine physisorption and chemisorption of hydrogen with an improved hydrogen binding energy. The material processing can be scaled-up, inexpensive, and approach some of the DOE targets.
- Investigators demonstrate high gravimetric capacities and durability.
- The project strength is the focus on the potential of inexpensive adsorbent materials. Also, it appears the project has attempted to make progress with little or no funding for this year.

Weaknesses

- PI does not recognize the fundamentals of the sorption process and hydrogen sorbent interactions.
- This reviewer doesn’t see good ideas behind the selection of doping materials. It is not clear if future progress can be made in improving the morphology of the carbon material.

- Reported gravimetric and volumetric capacities seem very high and do not seem to be consistent with other results in the literature. It is not clear what is so exceptional about this material to account for the unusually high capacities.
- The project weakness is the inability to provide the clear analysis execution.

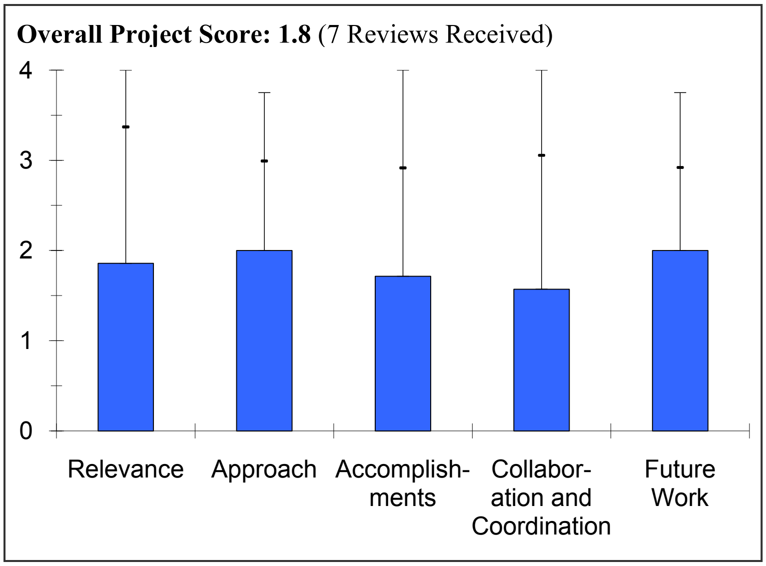
Specific recommendations and additions or deletions to the work scope

- Good characterization of the doping material (state, distribution, homogeneity) is necessary.
- Need to get sorption enthalpies (ΔHs) for all materials.
- Much improvement is needed to clearly identify the project plan. A more systematic study is needed to (1) use modeling to identify promising materials, (2) develop those materials, and (3) test the diatomic hydrogen storage properties. Instead investigators have developed a model for one material and then prepared a different material.
- Independent validation is necessary and should continue.
- No recommendations, this project has ended. [DOE note, this is an active ongoing project that has not ended.]
- A recommendation is not to add any scope, but concentrate the project's effort in developing and explaining the analysis techniques. The project should also provide a potential for improvement assessment to direct the next steps.

Project # ST-26: Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics

Robert P. Currier; Los Alamos National Laboratory

Brief Summary of Project



The objective of this project is to use applied electric fields to facilitate high hydrogen adsorption/loading under more economical ranges of temperature and pressure, with controllable uptake/release dynamics, and with moderate thermal management requirements. Features of the project include: 1) materials will be tailored to porous substrates with controlled dielectric response; 2) an electric field is applied across the porous substrate; 3) the field produces controlled, localized, dielectric response in the substrate; 4) localized polarizability should enhance hydrogen binding at those sites; and 5) upon discharge of what is effectively a "capacitor," the displacement field is removed, and, in turn, the energy binding diatomic hydrogen dissipates.

Question 1: Relevance to overall DOE objectives

This project earned a score of **1.9** for its relevance to DOE objectives.

- The objectives of this work are to use 10 to 20 keV potentials in a capacitor configuration in order to improve the normally weak electron correlations effects that promote adsorption of molecular hydrogen onto a surface. A 10 kJ/mole enhancement for the 2500 mole (or 5 kg) quantity implies a 25 MJ energy, which would amount to ~10% of the energy content of hydrogen. While not a bad number *per se*, some of this analysis, as well as the rationale for the 10 to 20 keV potential, would be in order. A gas in the presence of potential fields that are this high will invariable result in arcing and, conceptually, it seems puzzling that this work was funded. Given the overall 2,500-mole hydrogen storage requirement of this program, it is not clear that even in the absence of arcing, that the potentials suggested come close to the 0.1eV/molecule value required for enhanced sorption.
- This project at LANL speculates that the hydrogen adsorption capacities of metal-carbon systems might be enhanced by the presence of local, strong electrical fields from currently to-be-determined sources. There is minimal theoretical justification provided that sufficient bonding effects will be possible at practical field strengths or that the materials will remain stable in the presence of these fields. However, if significant hydrogen can be stored in the presence of an electrical fields, then the loss of the field would presumably give instantaneous desorption of the bound hydrogen, potentially generating high pressure in the storage vessel, which could rupture.
- It is quite surprising that this is even being funded given that: 1) it is impractical for a tank to have such high electric fields applied across it; 2) given the powder nature of most adsorbents (current technology), there is no way that you can polarize everything in a beneficial manner; and 3) any conductive path will neutralize the field.
- This is not a relevant technology, but is interesting on an atomic scale for academic purposes.
- This project is very relevant. Increasing the binding energy of metal-organic frameworks (MOFs) by additional physical binding is definitely a plus and is worth exploring.
- The project is relevant to the DOE storage goal of increasing physisorption storage capacity at room temperature.
- The project needs a conceptional device design and performance estimate to determine relevance.

Question 2: Approach to performing the research and development

This project was rated **2.0** on its approach.

- Again, the overall concept of this work is puzzling. The researchers themselves recognize from slide 6 that avoiding breakdown potential needs to be avoided. In any practical system, this will be impossible to do.
- The project consists of three main aspects: 1) development of a theoretical framework for the feasibility of enhanced hydrogen adsorption by localized metals in an organic host; e.g., MOFs, 2) preparation and dielectric characterizations of potential MOF compounds that could exhibit increased adsorption in the presence of strong electric fields, and 3) design and fabrication of a test system to perform initial feasibility demonstration experiments. A go/no-go decision point is scheduled in fiscal year 2010, but has not yet occurred. The test equipment is apparently not yet ready to permit any evaluations.
- The methodology and approach is actually reasonable. The combination of calculations and experiments are usually a good indicator, but the emphasis on detailed calculations to find the right material is a bit premature, given the fact that we do not really know if there is any improvement in well-known systems.
- Continuing from the previous sections, this is not a relevant technology for on-board storage.
- The approach is based on theory and experiment.
- The concept that applying a voltage-modifying, localized polarizability of high surface area materials should enhance hydrogen binding at those sites is interesting and attractive if possible. However, the R&D approach has been spread across diverse aspects of the whole storage concept. There does not appear to be enough focus on proof of concept testing that an applied electric field could actually cause significant changes in hydrogen storage capacity.
- The approach is generally unique; however, several key items need to be addressed given the high cost of this project.
- This project needs modeling components to predict device performance-even rough calculations. The project also needs to estimate the weight and size of a device and an upper limit on how much storage benefit one would get.
- Need an estimate of field (V/cm) needed to get desired increase in adsorption energy. What dielectric constant is needed?
- It is not apparent that investigators have really examined the criteria for success in this project. The team needs to set success criteria that would be needed for the technology to be relevant for improving hydrogen storage. Simply "increasing adsorption" does not equate to creating technology that will enable hydrogen vehicles.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **1.7** based on accomplishments.

- While there is a popular trend to view framework structures as a panacea to this program's goals, the implementation for the use of such a material in this application is not apparent. Even if as the PIs point out that linkers in the frameworks they have selected are more polarizable, to what extent is the localized polarization going to enhance uptake? This is a back-of-the-envelope calculation and should have been presented. Also, the synthesis of these materials is often imperfect, leaving remnant solvent in the framework structures and it is not clear how the collaborators who are responsible for this project will deal with this issue.
- Modeling results providing support for the concept were presented and several MOF compounds were apparently prepared while some materials were screened. A test system has been prepared, although initial experiments were not yet reported. Presumably, delays in funding to LANL on this project in early FY 10 has delayed their efforts.
- Given that the presentation is only a few slides in addition to what was presented last year, there is very little to judge this aspect on. They were rather slow on not only moving forward to do real experiments and get results and have very little direction on what kind of MOF would be most useful. The next go/no-go decision will be a crucial marker, and they do not seem to be close to proving if the concept works.
- Relatively fair progress given the funding delays and cuts. Presenters went into time-consuming details and efforts before establishing the validity of the concept, which was not preferable.

- Progress was made on determining dielectric response of test materials. Materials appear to have dielectric properties similar to other capacitor dielectrics. More focus is needed on demonstrating that hydrogen capacity can be enhanced (even marginally) for any of these materials by applying high voltage.
- Not much progress has been made, partially due to funding issues, but also due to the complexity of this project requiring a new measurement system setup.
- It appears that some very complex calculations are being done, but simple ones are not mentioned, such as: the field strength needed to attain 10-15 kJ/mole adsorption energy for a hydrogen molecule; given that number, whether there are dielectrics known that could be used in a device; how much the device would weigh; or how big it would be.
- Testing with carbon dioxide and argon show minimal effects. Need predictions from those results for hydrogen.
- The project team should consider breakdown voltages for MOFs.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **1.6** for technology transfer and collaboration.

- What is the division of labor amongst the collaborators? While the PI mentions ties through the "Chemical Center of Excellence," there is apparently no working relationship that the PI has with the CoE members. While LANL identified several outside organizations with some past collaborations, there was no indication that they were involved in this project. Also, there was no indication of interactions with any of the DOE-EERE partners involved with hydrogen storage technology.
- There seems to be some sample producing collaborations, but not much that is integral to pushing the research forward. A more detailed presentation indicating how the collaborators interact could help improve this perception.
- The project has yet to be effectively established. They really need to interact with some adsorption experts; they could save lots of effort and time.
- Collaborations show a lot of strength in the area of materials development. More collaboration is needed with institutions that have expertise in precise hydrogen sorption measurements.
- No visible collaboration seems to exist outside of obtaining materials for their system.
- Partners listed, but no indication of their level of involvement in the program is given.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.0** for proposed future work.

- There are a number of "cart-before-the-horse" plans that the PI has proposed over the next 2 years. Because of the difficulties the reviewer has with the overall concept of this project, any work toward attempting to execute the work as outlined in the proposed work seems to be of rather limited value.
- Among all the tasks described in the future plans for this project, the most critical should be experimental tests on current samples to see if there are enhancements of hydrogen adsorption in the presence of strong electrical fields. Preparation for the go/no-go decision is paramount.
- The FY 10 go/no-go decision must be adhered to.
- The project really needs to primarily prove concept in a simpler way.
- Addressing validation of enhanced capacity has been identified as the first topic for future work. The majority of effort should be focused on this. Understanding the effects of adsorbed impurities on the electrical properties of the test materials by comparison with baked-out samples is lacking.
- It is recommended to relate the project to the well-to-tank efficiency earlier on, in order to establish feasibility. Scoping and clear goals are needed to guide future work. For example, if increased adsorption is demonstrated under a set of conditions, investigators should extrapolate data to estimate conditions required for the technology to be commercially relevant.

Strengths and weaknesses

Strengths

- None.
- A potentially innovative concept if something can be demonstrated via laboratory tests and not just theoretical rationalization. Search for specific types of MOFs with metal atoms that might provide the desired effects.
- Sample environment and measurement capabilities are interesting and could be useful to answering some of the overall questions concerning the premise.
- Novel approach.
- Good collaborations with materials developers. If concept is valid, then it will open up a whole new approach to hydrogen storage.

Weaknesses

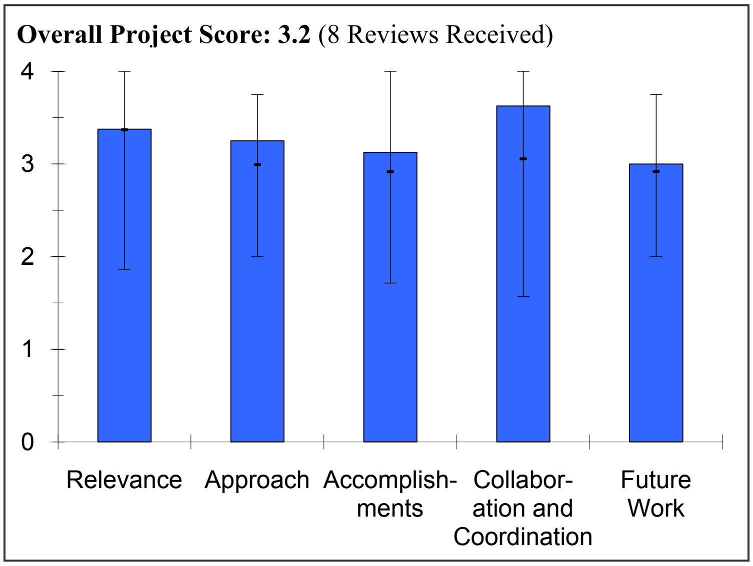
- The PI has vastly underestimated the potentials that are required for this work. Even working with the potentials that the PI has assumed will be adequate, these potentials under modest pressures will result in gas breakdown with arcing.
- There does not appear to have been any detailed assessment of the electric field strength necessary to provide for the behavior desired. The theoretical arguments are not convincing as presented at the AMR.
- There are no plans to observe, atomistically, the effects of electric fields. They need diffraction or clear well-known techniques to prove that this works over all the sample and is not a zero-sum game where the field can aid adsorption in one direction but hurts it in the opposite.
- Difficult to implement in practice.
- Too much focus on supporting science (modeling, synthesis, safety, and materials properties) without sufficient evidence that the basic principle is valid. More collaboration with experts in accurate hydrogen sorption measurements needed.
- Efficiency concerns were not addressed.
- Hydrogen molecule potential dissociation not addressed (technical hurdles).
- Safety issues were not addressed.
- There is a lack of focus and clear goals that would enable commercialization.

Specific recommendations and additions or deletions to the work scope

- This project needs to be scaled back in a substantial way. If the PI wants to prove the concept, this needs to be done with less exotic materials.
- The project should focus on preparing for feasibility demonstrations in the laboratory as quickly as possible, spend less effort on theoretical predictions, and perform tests.
- Concept of the benefit of capacitance electrical energy storage and re-adsorption of hydrogen with regenerative braking should be validated with simple calculations.
- Energy loss in maintaining a large differential voltage for a vehicular storage system may be a serious problem. This should be addressed with simple, small-scale measurements on current test materials.
- Decomposition of MOF and other materials in the presence of hydrogen at a high voltage may make these materials impractical for reversible hydrogen storage. Simple voltage cycling of samples in a hydrogen environment could be performed with material characterization (X-ray diffraction) to evaluate whether materials will withstand such cycling.
- Without illustrating the feasibility potential very soon, at least based on estimation results and current data, it is recommended to delete this project.
- Scoping work.

Project # ST-27: Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis Using Ordered Polymer Templates

Mark Allendorf; Sandia Natioinal Laboratories



Brief Summary of Project

The overall project objective is to achieve tunable thermodynamics for hydrogen storage materials by controlling nanoparticle size, composition, and environment. The key goals for fiscal year 2009 are to: 1) demonstrate and downselect infiltration methods, 2) measure desorption kinetics for simple and complex hydride nanoparticles, and 3) benchmark density functional theory and atomistic nanoparticle models using Quantum Monte Carlo (QMC) to quantify the effect of nanoparticle size on the enthalpy of reaction (ΔH°_d) and develop a compositional tuning method.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Destabilizing of complex hydrides that are usually too stable to release hydrogen under moderate pressure and temperature is a key issue. This project strongly supports the Hydrogen Program.
- The project is relevant to DOE objectives and explores tunable thermodynamics for hydrogen storage materials by controlling nanoparticle size, composition, and environment.
- This project seeks to develop a fundamental understanding of the behavior of hydrides confined within nanoporous templates. The work is motivated by early research, which shows that for some hydrides, nanostructuring stabilizes the hydrides while in others, nanostructuring destabilizes the hydride. The researchers are taking a very systematic approach to scaling hydrides within the range of 1-15 nanometers (nm). This understanding is well within the DOE scope for improved kinetics. However, the ability to scale-up the most promising nanoconfined structures in a cost effective manner remains at question.
- One of DOE's objectives is seeking materials that will absorb and release hydrogen under specific temperature and pressure conditions. The proposed research in "tuning" the thermodynamics is extremely relevant to this objective.
- This project clearly supports the Hydrogen Program and DOE research, development & demonstration (RD&D) goals and objectives for fuel cell vehicles. It is compactly focused on one central theme—using nano-confinement techniques to destabilize metal hydride-type hydrogen storage materials. In this sense the project directly addresses the central issue for effective utilization of metal hydrides for on-board fuel storage.
- Prohibitively slow sorption kinetics and large reaction enthalpies, especially in many complex hydrides, are serious obstacles to the successful incorporation of those materials in a practical storage system. Understanding the role of nanoparticle size on the thermodynamics and kinetics of hydrogen sorption reactions using the novel approach employed in this project is an important component of the DOE RD&D program and is directly relevant to DOE needs and objectives.
- The project's objectives are well aligned with the DOE Hydrogen Storage Program.
- The AMR rating criteria for relevance is clearly not appropriate for this particular project; its numerical rating unfortunately suffers from that fact. It does not quantitatively and directly discuss the DOE targets and the potential for meeting them, and should not be expected to. It is a very fundamental project aimed at testing the speculations and calculations that low nanometer particle sizes can result in thermodynamic

destabilization of stable hydrides like magnesium hydride, lithium hydride, etc. If successful, this would be an interesting and valuable scientific finding, but it would not be expected to result in practical engineering systems in the near to medium term.

Question 2: Approach to performing the research and development

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

- It is significantly important to identify the "size effect" using a computational method before designing the size of scaffold for hydrogen storage materials to be placed. In the experimental part the project is ready to use a wide range of pore sizes for the research.
- The approach of the project is to use different templates such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), zeolitic immidazolate frameworks (ZIFs), and block copolymers to create nanoparticles by infiltration, reduction, and stabilization. The experimental synthesis work is supported by theory (density functional theory (DFT), Quantum Monte Carlo (QMC), and nano-prototype electrostatic ground states (NanoPEGS)) and characterizations.
- The approach involves synthesizing the pore structure, confining the hydrides within it, and characterizating the materials before and after desorption of hydrogen. This is a very solid and systematic approach.
- In particular, the systematic variability of size has led the researchers to determine, that for lithium borohydride, particles below a 7-nm size, have desorption behavior that is very different relative to particles above that size.
- The approach of infiltrating metal hydrides into novel organic frameworks is innovative and well conceived. The assumption that nanoparticles could be contained in the pore structure of MOFs, and that this may affect thermodynamics, is logical.
- The project is indeed well designed, feasible, and integrated with other related efforts. The approach has both depth (detailed study of specific destabilization methods) and breadth (looking at a variety of promising confinement media). The quality of the synthesis, testing, and characterization science is very high.
- This project uses ordered polymer frameworks as nanostructure-directing agents for generating hydride nanoparticles. This is a novel approach that is allowing the team led by the Sandia National Laboratories (SNL) to probe the effects of nanoparticle size on sorption thermodynamics and kinetics in a systematic way. To my knowledge, this is the only project within the DOE program that is investigating these effects using particles with well-controlled sizes.
- Although the approach is innovative, there are limitations, especially with regards to unwanted interactions between (some) hydrides and the ordered polymer template. This can deleteriously affect the sorption reaction characteristics. Also, the stated objective of the project is to “achieve tunable thermodynamics…by controlling nanoparticle size…” However, in this reviewer’s view, it is far more likely that reaction kinetics will be altered. Separating those effects in reactions employing very small sample sizes is a challenging experimental endeavor.
- The approach is unique in that it aims to improve the thermodynamics and kinetics of previously known chemical hydride materials by encapsulating nano-size particles in the pores of carbon templates such as MOFs.
- The use of polymer templates for making ultrafine hydrides by infiltration techniques is an interesting and new approach.
- The theory on nano-sized hydrides has long been in confusion; it would be good if this project could resolve that problem once and for all. Having said that, there is relatively little thermodynamic-based diatomic hydrogen desorption/absorption testing relative to theory and other non-thermodynamic measurements.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- A wide range of scaffold have been readied. Using scaffolds some differences have been observed comparedto the materials without scaffolds, but it seems to be kinetic phenomena and not destabilization of materials. In other words, control of thermodynamic properties has not yet been shown.
- Template materials providing a 1- to 20-nm range of pore sizes were prepared. Infiltration with metal hydrides was studied for a number of hydrides. Formation of infiltrated hydrides and their destabilized behavior was demonstrated. Application of modeling (DFT and QMC) was critically evaluated.

- There was no clear delineation between work done prior to this funding year and during this funding year. However, assuming ALL of the work presented was a part of this funding year, the results are many.
- Specifically, the research group has investigated the stability of MOFs (used as templates in some cases) and has revealed a difference in the behavior of copper-based MOFs used relative to zinc-based MOFs (which degrade at desorption temperatures for the hydrides).
- The research group has transmission electron microscope (TEM) tomography results, which show the presence of hydrides throughout the pore structure; i.e., filling of the 1- to 15-nm pores with hydrides).
- There has been some significant progress toward achieving the goals set forth in this project. It is noteworthy that the hydrides are compatible with the MOFs but not with ZIFs. It is also noteworthy that some of the hydrides have shown reduced desorption temperatures when in the MOFs. Some kinetic data has been presented, but nothing in the way of thermodynamic data has been presented.
- Excellent progress has been made toward goals and objectives. Examples include the following:
  - Templates in the 1- to 15-nm size range have been synthesized.
  - Confinement of particles as small as 1.5 nm diameter has been archived.
  - Observed enhanced desorption in sodium aluminum hydride/MOF vs. bulk.
- Solid results have been obtained on preparation of appropriate templates (especially MOFs, block polymers, and resins) with well-controlled pore size. Good results have also been obtained from the modeling of high symmetry clusters and from understanding the limitations of the modeling approaches for understanding nanoscale hydride behavior in ordered templates.
- The successful demonstration that a metal hydride is compatible with an MOF template upon infiltration is an important first step toward the development of controlled nanostructures. However, the degradation of ZIFs with hydride incorporation underscores the sensitivity of the template materials to successful formation of the hydride nanostructures. Also, serious caution must be exercised in interpreting results that may be compromised by the formation of chemically tenacious adducts that have proven to be problematic during solvent-based infiltration of aerogels with hydride compounds.
- Results obtained on sodium aluminum hydride nanostructures formed by melt infiltration into cylindrical pore carbon seem to be similar to results on much larger particles formed by infiltration into aerogels (HRL Laboratories and United Technologies Research Center (UTRC) work). The questions remain to if there a measurable pore size dependence and are these particles really small enough to show a change in thermodynamics, and, if so, how the can surface effects be ruled out.
- The synthesis and infiltration technique of the hydrides in the nanoporous carbon templates has been demonstrated.
- The project's hypothesis is verified by the lower desorption temperature observed in some systems.
- With the project nearly 60% completed, uncertainty seems to dominate still.
- Various theoretical approaches are giving contradictory or negative results. It seems there is little time left in the project to complete the theory, much less accomplish experimental confirmations.
- The one experiment purporting to show nanoparticle destabilization (sodium aluminum hydride, slide 10) really shows kinetic improvements, I believe, not thermodynamic destabilization. Sodium aluminum hydride is already thermodynamically unstable at room temperature. Positive fine particle effects on kinetics have been shown in many, many papers.
- To their credit, investigators have shown a great versatility in making templates and infiltrating them with hydrides.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.6** for technology transfer and collaboration.

- Collaboration between computational and experimental people is excellent.
- The project has an extensive network of first-rate collaborators, both in computational modeling, experimental work, and characterization.
- The project is a collaboration among six different institutions. This broad collaboration permits the avaibility of specialized characterization tools (including neutron scattering) and computational research (including DFT and QMC).
- More reuslts from the nuclear magnetic resonance (NMR) and neutron characterization "branches" of this project should have been included within the presentation. This is an area suggested for future improvement.

- There is an impressive list of active partners in this research who are making significant contributions.
- Collaborations seem appropriate and well coordinated. Roles and responsibilities are clearly established. The project leaders reached all the way to Germany to bring in unique expertise. Research on the synthesis of confinement media is at a very high level. The overall approach to characterization is also impressive.
- There is excellent synergy between theory and experimental work. Significant contributions have been demonstrated by all team members. This is a well-coordinated research effort.
- There is a good collaborative plan in place.
- There are several very well-qualified collaborators, but they seem to be mostly experts in theoretical approaches and non-hydrogen experimental measurements. It is not clear who is doing the work, if any, on measuring thermodynamic properties (pressure-composition isotherms (PCT) and van Hoff analyses).

Question 5: Approach to and relevance of proposed future research

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

- The size criteria that is the border of the bulk and cluster has been clarified for some of materials. The next step will be to prepare the appropriate sample smaller than the criteria in a scaffold.
- Many experiments were proposed for future study—including a delineation of size effects at the smallest range, i.e., between 1 and 5 nm. Researchers suggest differences in behavior as size scales from 1 to 5 nm, but more experiments are needed to verify this.
- The proposed future work is reasonable. They plan to continue with the synthesis of the hydride and MOF combinations and to do the thermodynamic and kinetic studies.
- The future plans clearly build on past progress and are sharply focused on the pivotal technical barriers for metal hydrides. The individual tasks are neatly connected. The project is designed to either succeed, or at least determine with confidence, what the performance limits are going to be for metal hydrides.
- Future plans address the important issues that have been raised thus far in the project. The go/no-go decision in 2009/2010 for the compositional tuning effort is appropriate. It will be important to focus on cycling and the extent to which reversibility can be demonstrated in the nanostructures compared with results obtained in bulk materials.
- Future plans should include a quick assessment of the proposed system to meet the DOE hydrogen storage targets.
- Though not specifically addressed by the project team, it is clear from the results that there is a huge trade-off for their proposed approach; namely, improved desorption kinetics at the expense of drastic reduction in storage capacity. There should be a go/no-go decision point for the calculated theoretical limit in storage capacity of an ideal system.
- The remaining work proposed for the remainder of this project seems like more of the same.
- Future plans (slide 17) say nothing about experimental determinations of thermodynamics. The section "dehydrogenation thermodynamics and kinetics" on slide 17 talks only about kinetic measurements. "Tunable thermodynamics" (contained in the title) should be at least half of the "dual approach" of this project.

Strengths and weaknesses

Strengths

- The project firstly identifies the border of bulk and cluster by calculation. Then, it synthesizes the clusters in various scaffolds following the computational achievements.
- The project develops a new type of material based on tightly dispersed nanoparticles of hydrogen-absorbing phases. It has the potential to overcome kinetic and thermodynamic limitations of these phases to achieve characteristics desirable for hydrogen storage applications.
- The researchers use a very rational approach to tune the properties of hydrides via nanostructuring. This is commendable—results are many and impressive.
- The project team consists of a group of well-qualified scientists with the expertise needed for the project.
- The project has strong leadership, creative approaches, and world class investigators.
- The project has an extremely capable experimental and theory team. A novel experimental approach is being employed that has the potential to provide in-depth understanding about important research issues concerning the effects of nanoscale structure on thermodynamics and kinetics of metal hydride sorption reactions.

- Hydride encapsulation synthesis capabilities have been demonstrated.
- There is good collaboration in material characterization and accompanying computational methods.
- The PI and collaborators have good theoretical expertise.

Weaknesses
- At present, real destabilization has not been found. It is uncertain if the methodologies to synthesize the cluster are under precise control of the size as the computation predicts.
- The project needs better TEM and electron energy loss spectroscopy (EELS) work for direct verification of dispersion of phases and their crystallographic characteristics. Not sure what "Wulff construction" is. If it is a shape of minimal surface energy facets, the PI should state whether it determines stability. the reviewer questions if "Wulff construction" a macroscopic concept and therefore not applicable to nanosize particles.
- There seems to be some confusion as to whether thermodynamics are tuned or if kinetics are varied by nanostructuring. To date, the researchers have yet to sort out this issue. One of the major barriers is the synthesis of enough nanoconfined material for measurement via Sievert's apparatus (or similar) to yield thermodynamic data. The difficulty which arises in attaining enough nanoconfined materials for the purpose of thermodynamic measurement also leads this reviewer to question the ability to scale-up the approaches to commercially viable and cost effective techniques (if a system is identified to be promising for meeting DOE targets).
- The integration of NMR and neutron scattering techniques are not complete.
- No progress has been made on the thermodynamics. An effort should be made to determine if the materials absorb and release hydrogen reversibly while infiltrated into the MOFs.
- None are apparent.
- A more complete description of obstacles and barriers to achieving controlled nanostructure dimensionality is needed. In these experiments it has been challenging to discriminate between kinetic and thermodynamic effects. A comprehensive research effort that provides a compelling pathway to understand these differences is needed.
- The trade off in hydrogen storage capacities of proposed infiltrated systems not addressed at all. This can potentially be deterimental to the project's success.
- Diatomic hydrogen measurements are too weak and limited, so far, to confirm theoretical predictions (the PI admitted this during the question and answer part of the presentation).

Specific recommendations and additions or deletions to the work scope

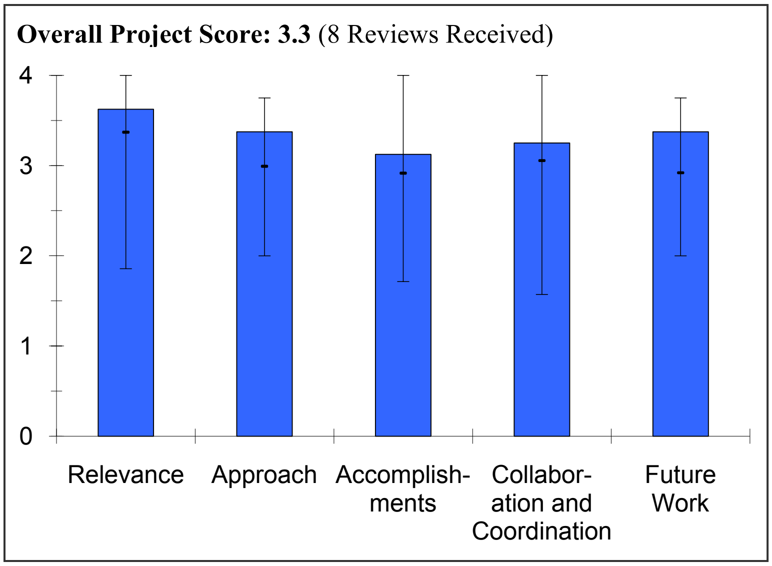
- The original idea is excellent, but how to make it real seems to be a little bit weak. There have been a lot of the similar kind of attempts using various materials, however, to make nano particles smaller than a few nm is critical.
- No recommendations for additions or deletions—only a suggestion to more fully integrate the existing tools; i.e., NMR and neutron scattering) with synthesis work.
- Stay the course. I wouldn't change a thing.
- Greater emphasis on discrimination between kinetics and thermodynamics effects in hydrides should be incorporated in nonporous materials. Focus on drawing a definitive conclusion about the changes in sorption reaction properties as a function of particle size.
- It may be useful to consider supercritical fluids as solvents (as in work by Jensen, et al.) to facilitate hydride infiltration. That approach could avoid the formation of stable adducts which can confuse interpretations of results.
- Carry out a quick theoretical calculation of combined physi-sorbed and chemi-sorbed capacities of idealized systems to determine the potential of the proposed approach to meet DOE targets in order to justify further work on this pathway.
- Make pressure-composition-isotherms (PCT) measurements to quantify thermodynamic changes, if any (the PI strongly promised to respond to this need).

Project # ST-28: Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

Christopher Wolverton; Northwestern University

Brief Summary of Project

Three materials classes: chemical, metal/complex, and physisorptive have been divided into DOE Centers of Excellence (CoE). The overall objective of this project is to combine materials from these distinct categories to form novel multicomponent reactions. Systems to be studied include mixtures of complex hydrides and chemical hydrides; e.g., $LiNH_2 + NH_3BH_3$, and nitrogen-hydrogen-based borohydrides; e.g., $Al(BH_4)_3(NH_3)_3$. These types of combinations have only recently begun to be explored, but initial results look very promising.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- Computational approach to develop novel hydrogen storage materials is one of the ideal ways, but it is very challenging.
- The project is relevant and may be critical to ultimate DOE objectives–finding light reversible hydrides.
- This project does an excellent job of computationally narrowing down reaction pathways in combined boron and nitrogen containing hydride mixtures. However, the computational work is very far ahead of the experimental synthesis work. This may be because the start date (a little over 1 year ago) has been only enough time for the computational branch to develop a system of proposed reactions to be pursued experimentally.
- This project does fully support the Hydrogen Program and DOE research, development & demonstration (RD&D) goals and objectives. It offers the possibility to identify and test new hydrogen storage material concepts with the potential to meet on-board storage system performance targets.
- This project is exploring a new class of multi-component, complex hydrides for reversible and non-reversible hydrogen storage applications. It directly complements work that has been performed at the Chemical Hydrogen CoE (CHCoE) and the Metal Hydride CoE (MHCoE). Specifically, the project explores compounds from different CoE material categories. This comprehensive, cross-cutting study is exploring novel material mixtures in a new way. The project is well-aligned with DOE RD&D objectives for hydrogen storage.
- The project is relevant in that it aims to understand the physical and chemical as well as the charging and discharging properties of multi-component hydrogen storage systems made up of various hydride systems.
- The project aims to meet DOE objectives and barriers such as weight, volume, and rates. In fact, the focus is mostly on weight, with nothing on volume.

Question 2: Approach to performing the research and development

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

- Experts working on this project utilized the most advanced software for exploring novel hydrogen storage materials.
- The project approach combines powerful and tested computational methods with experimental verification of the validity of the theoretical predictions.
- The researchers have developed a systematic approach to combine borohydride and ammonia containing systems (and to explore many compounds and their associated reactions). The researchers also suggest that

another level of tunability can be achieved by changing the cation on the system (and the researchers have moved to include calcium cations).
- This project is indeed sharply focused on the key technical barriers for on-board hydrogen storage. The basic approach is to combine candidates from the three distinct categories of hydrogen storage material types (chemical, metal/complex, and physisorptive) to form novel multicomponent reaction media. The hope is that some special thermodynamic and/or kinetic synergies will unfold that will bring hydrogen storage capacity and diatomic hydrogen uptake and release performance into the range needed to meet on-board storage system targets.
- This project employs both experimental and computational modeling methods to explore novel multi-component reactions of (primarily) light metal complex hydrides and nitrogen-based borohydrides. The large array of reactions that can be assessed using these starting materials, as well as the potentially high gravimetric and volumetric storage capacities that can theoretically be achieved, make these compounds especially interesting candidates for reversible and non-reversible hydrogen storage applications.
- The experimental studies and theory work are strongly coupled, and a well-formulated plan is in place to converge on the most promising candidates. The division of effort (computational prediction, measurements, and kinetics/catalysis) provides a good way to efficiently identify and test new systems. However, as with most complex hydrides, the problem of prohibitively slow kinetics remains a serious challenge. Only limited attention is given to this critical problem.
- This reviewer is not clear what the scientific basis behind the project's approach is. It appears like the PIs are hoping to find success by mixing X and Y, even though they are aware X or Y separately is not the material of choice!
- The approach is very sound, namely the use of various theoretical calculations to predict new reactions and materials that might result from mixing two or more classes of hydrides.
- The intent to follow up on theoretical predictions with experimental confirmations is a critically important part of the plan.
- The project, at least as planned, is an attractive combination of theory, experiment, and original equipment manufacturer (OEM) needs.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- Thanks to prototype electrostatic ground state (PEGS), that does not need crystal structure data for performing density functional theory (DFT) calculations, computational results can predict novel materials with their structures. The presentation showed the splendid agreement of their computation results to experimental ones nicely.
- Significant progress was made in predicting new compounds and reaction paths, and finding their energies.
- The work on catalysts is not very clear to the reviewer.
- Many computational results were presented, and the most promising reactions were narrowed down. However, the experimental results development seems to lag behind the computational developments. This should be corrected for next year.
- Progress has been significant considering the amount of work done and the nature of the findings to date. The coupling of theory and experiment is carried out very nicely in this project. What has not yet happened is finding the loadstone combination of materials that actually and demonstrably overcomes the barriers that the project is addressing.
- This project is off to a good start. Computational screening has identified a large number of multicomponent materials from several material classes whose predicted thermodynamic and storage capacity properties make them potentially viable storage candidates. The experimental effort is obviously just ramping up, but some interesting preliminary results have been obtained.
- Although they are undoubtedly recognized by the project team, three important issues must be addressed: 1) in many related systems, even though the predicted and measured thermodynamic properties seem to suggest that the materials might be ideal, slow sorption kinetics limit the system to operation at high temps and pressure; 2) in the nitrogen systems, ammonia generation is always a concern,; and 3) reversibility and high capacity cycling are often problematic in systems comprising multi-step reactions. Solid plans should be in place to address these issues.

- There is a well defined combinatorial discovery approach for a difficult area of research.
- The project has identified metal amidoborane systems with reasonable theoretical capacity and enthalpy.
- Several new and potentially interesting hybrid materials were predicted by theoretical calculations.
- Unfortunately, the experimental side of the effort seems to be lagging behind the calculation side. There were only a few experimental confirmations attempted, usually just temperature scans without formal dehydriding capacities, thermodynamics, or kinetics obtained.
- Most of the materials studied were based on mixtures of hydrides, borohydrides, and amides with significant potential for the generation of impurity gases; e.g., boranes and ammonia. Impurity problems were acknowledged with only vague paths suggested for mitigation.
- The new possibilities are certainly impressive in terms of gravimetric hydrogen capacities, but not a word was said on the volumetric capacities.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- The distinguished scientist who developed PEGS is an "outside collaborator," but without PEGS, this project cannot stand.
- Collaboration with experimentalists seems to be ideal.
- The project will need to add a strong synthesis and experimental partner.
- The project has an extensive network of collaborators, both in computational modeling and in experimental work and characterization.
- The research project is a synergy between experimental and computational groups with the focus on developing new hydrogen storage materials and on enhancing kinetics via catalysis of those materials once developed. This is a very strong strategy.
- Many computational results were presented and the most promising reactions were narrowed down. However, the experimental results development seems to lag behind the computational developments. This should be corrected for next year.
- Partnering or collaboration within this project is well organized and appropriate, as are the links to the Hydrogen Storage Engineering CoE. The roles and responsibilities are clearly established and coordination of research tasks; e.g., theory and experimental validation, appears to be going along nicely.
- Close collaboration among highly qualified experimentalists and theorists is evident. The “in-depth automotive perspective” is an important element of the overall technical interaction.
- The roles of the partners are well defined and complementary.
- The effort seems to be a valuable collaboration among theoreticians, experimentalists, and OEM users. However, it is not clear if and how the collaborations are functioning. For example,it is unclear if the OEM participant is providing input to support the belief that these newly predicted compositions have reasonably near-term value.

Question 5: Approach to and relevance of proposed future research

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

- The way of thinking is very clear and the leadership of the PI is excellent.
- This reviewer would like to see not just the lowest energy reaction; higher energy reactions cannot be discarded because they can be realized experimentally for kinetic reasons. Attempting to understand the kinetics of the proposed reaction is very desirable.
- The compounds of interest must be synthesized and the reaction pathways explored. The experiments will verify these reactions using infrared (IR) spectroscopy and X-ray diffraction. This is a good plan for future work.
- The future plans build logically on what has been accomplished to date and remain sharply focused on the key barriers to on-board hydrogen storage. These plans include the following studies:
    - Extend computational search for promising reversible reactions in a lithium-calcium-boron-nitrogen-hydrogen system.

  - Characterize storage properties/reactions of $(NH_4)_2B_{12}H_{12}$.
  - Extend catalyst studies to $(NH_4)_2B_{12}H_{12}$.
  - Continue computational search for 1) novel borohydride/amine compounds and reversible reactions, 2) mixed metal borohydrides, and 3) ammonia borane reaction products.
- The future plans are well formulated, and they provide a good pathway to achieving project goals. However, primary emphasis seems to be on identifying and testing candidate materials having satisfactory thermodynamic properties. Less attention is being paid to kinetics issues (slow kinetics in these systems seem unlikely to be solved by catalysts alone). It is recommended that future plans include more serious computational and experimental efforts on the kinetics problem. In general, the principal obstacles and barriers that are currently perceived should be articulated, and a fairly detailed plan for how to deal with them should be in place.
- Proposed future research is reasonable. It should be made clear that the needed experimental verifications of predicted materials will be accelerated.
- Because this approach involves intermediate stage calculations and predictions, it would seem that it would be more useful in predicting kinetics, not just end-point thermodynamics and weight percentages. This potential future work effort seems to be missing. (During the question and answer part of the presentation, the PI expressed doubt that can be accomplished at this time).

Strengths and weaknesses

Strengths

- Utilizing the PEGS program, novel hydrogen storage materials can be predicted. Collaboration between computational and experimental scientists is ideal.
- The project combines powerful state-of-the-art computational methods with experimental verifications.
- Validity of the approach is validated by a number of successful discoveries.
- The research plans take a systematic approach to examining a large number of systems and reaction pathways.
- The computational results presented are impressive.
- The project incorporates a knowledgeable PI, experienced scientific partners, and a reasonably novel approach (something not tried before).
- The project has a strong team that has all of the requisite computational and experimental capabilities to make good progress on this challenging project. The project uses novel ideas and provides good opportunities for exploring a new parameter space of materials.
- The computational methodology used is excellent.
- Excellent theoretical capabilities.

Weaknesses

- The developer of PEGS is outside of the project.
- The project should consider other reactions than just the lowest-energy reactions. More experimental validation work is desirable. It is not clear what to do when the phases are liquids or amorphous. The lack of kinetics studies in this project seriously undermines the power of the predictions made.
- As said before, the experimental validation appears to lag, somewhat, behind the computational group. This will likely correct itself in year 2 as the computational group delivers promising compounds for the experimental groups to explore.
- None that are obvious.
- Insufficient emphasis on kinetics issues. Slow kinetics have been found to be a serious problem in related complex hydride systems. A cursory study of catalytic effects seems unlikely to provide the guidance needed to satisfactorily address the kinetics challenges.
- There is too much reliance on computational modeling.
- Experiment lacks modeling work.
- System complexity and reversibility challenges are not adequately addressed.
- Project does not have go/no-go decision points.
- The researchers are not following the theoretical (calculational) work with more immediate experimental hydrogen confirmations, which are preferred.

Specific recommendations and additions or deletions to the work scope

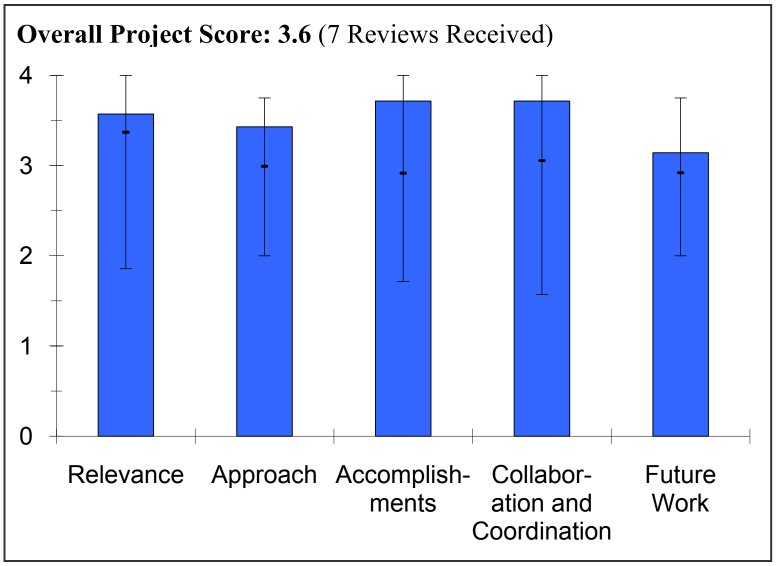
- The scientist who is still developing PEGS, and therefore needs good supports, should be included as a project partner or given financial support from the project. As far as this reviewer's understanding, the PEGS program has not been opened to the public, but only a small number of users are currently able to use it.
- This project will benefit greatly if it can organically align itself with an experimental or synthesis project in metal hydrides such as project ST-032. There are some strong synergies between these two programs.
- No recommendation for additions or deletions. The project can be improved by developing supporting experimental data (as already planned by the researchers).
- Try to steer away from reaction paths that end up with final products like boron that are hard to regenerate.
- Combinations that mix physisorbers with chemical and/or metal hydride storage materials should be considered.
- Future plans should focus more strongly on enhancing sorption kinetics. Also, unwanted generation of ammonia in nitrogen-hydrogen containing compounds should be addressed more thoroughly, and strategies for inhibiting ammonia formation should be explored (the statement that “ammonia liberation could be reduced by optimization of composition” is too general—a more detailed description of the approach is needed).
- Verify that the new low temperature hydrogen release is not the result of a simple disproportional reaction of sodium amide. Consider running temperature-programmed desorption mass spectrometry (TPD-MS) on sodium amide alone under the same conditions.
- More in-house or partner measurements on dehydrided diatomic hydrogen purity and a greater focus on mitigating that problem is needed.

Project # ST-31: Advanced, High-Capacity Reversible Metal Hydrides

Craig Jensen; University of Hawaii

Brief Summary of Project

The overall objective of this project is to develop a new class of reversible complexes that has the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets. Current investigations include: 1) magnesium borohydride nano-confined carbon aerogels; 2) reversible dehydrogenation of high capacity borohydrides at low temperatures; and 3) development of a method for the hydrogenation of lithium hydride/aluminum to lithium aluminium hydride at moderate conditions in unconventional solvents.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- The project is exploring new reversible metal hydride (MH) materials, which is a critical pathway for the program.
- The reduction of cost and the increase in kinetics and high capacity materials all allign with the goals of the program. The underlying concern for cost is very good.
- This project strongly supports the Hydrogen Program and DOE research, development & demonstration (RD&D) goals and objectives. The work is focused on the types of materials that (arguably perhaps) have the best chance of meeting the on-board hydrogen storage targets. The emphasis on new confinement approaches and new solvent embodiments separates this work from what has been done in the past with the same families of storage materials.
- The project is fully relevant to the DOE Hydrogen Program mission.
- The project is generally in line with DOE objectives and targets. Weight and reversibility at reasonably mild conditions is emphasized. Some nominal volume calculations would have added to the project's usefulness.
- The project is relevent to the discovery and optimization of novel on- and off-board reversible metal hydrides. This project really tries to tackle the key challenges associated with materials as opposed to going after "low hanging fruit."

Question 2: Approach to performing the research and development

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

- The approach is based on the PI's vast technical expertise, network, and experiences.
- Multipronged program with several ways to succeed.
- Scaffolding methods are good for kinetics, but are not so good for mass and volume.
- The magnesium borohydride work was excellent, no one had done that before.
- Regeneration using supercritical fluids is a standard (low-cost) approach to other problems and is a good way to proceed.
- The University of Hawaii project is now honing in on a select few of the more promising storage materials coupled with some novel utilization concepts. Specifics of their approach include:
    - Magnesium borohydride nano-confined in carbon aerogels.
    - Reversible dehydrogenation of high capacity borohydrides at low temperatures.

  - Development of methods for hydrogenation of lithium hydride/aluminum to lithium aluminum hydride under moderate conditions in unconventional solvents.
- Excellent approach.
- The effort is chemistry oriented and aims to improve a very diverse range of hydrides. One might argue the effort is too scattered, but, because of the PI's extensive collaborations, this approach works out very well.
- The approach, in the most general sense, appears to be the utilization of novel chemical approaches for the exploration of reversible and non-reversible metal hydrides. While this very general approach is being successfully applied, there is not a clear thread that links the various storage systems. It was great to see an increased focus on select storage systems verses previous years.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.7** based on accomplishments.

- This project has consistently provided new materials and approaches.
- The project has gotten a lot accomplished in several areas. It was able to get magnesium borohydride into a scaffold, but the big problem, reversibility, was not solved. They achieved 4.28% total, including the scaffold and a huge temperature reduction. However high-pressure and temperature settings did work for reversibility, which was a first for that compound.
- Dimethylether (DME) was used as a liquid with a catalyst to regenerate lithium aluminium hydride. They looked at energy of regeneration, a very nice thing to have done.
- Progress toward meeting goals and objectives was impressive in the past year. Some key results are listed below:
  - Achieved high (60 wt %) loadings of magnesium borohydride in carbon aerogel.
  - Demonstrated that nano-confinement of magnesium borohydride improves dehydrogenation kinetics, but does not change re-hydrogenation pathway.
  - Reversible hydrogenation of magnesium diboride to magnesium borohydride achieved for 12 wt% hydrogen.
  - Reversible partial dehydrogenation of magnesium borohydride achieved under mild conditions.
  - Obtained fully charged titanium-doped lithium aluminum hydride in major yields from direct hydrogenation of titanium-doped lithium hydride/aluminum in liquefied dimethyl ether at room temperature under 100 bar of dimethyl ether.
- The rehydrogenation of metastable alanates in liquified dimethyl ether is a creative approach and the results obtained are very good.
- Very good accomplishments.
- Much has been accomplished in this diverse project, including several old materials made more practical in terms of synthesis and reversibility.
- Unfortunately, the synthesis of aluminum hydride in supercritical fluids (the main intent of the project originally) did not work out, but the PI has abandoned that and has moved, credibly, in a number of useful alternative directions.
- The full reversibility of magnesium borohydride has apparently not been accomplished below the severe conditions of 400˚C and 900 bar. Given the borohydride cluster problem, it was a good try that may set the stage for success some day with this interesting material.
- The synthesis of lithium borohydride from lithium hydride and aluminum-titanium in dimethyl ether is a very positive development.
- Overall, very good progress is being made for a variety of storage materials and reactions. This progress also broadly covers the areas of kinetics, reversibility, regeneration, and discovery. In particular, the most valuable and interesting results are demonstrating reversibility in magnesium borohydride, successfully incorporating metal hydrides into scaffolds and looking into regeneration for lithium aluminium hydrides.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.7** for technology transfer and collaboration.

- This project has always maintained a very diverse network of collaborators.

- Work performed with several partners. Partnerships, in part, drove the work.
- The PI is perhaps the most connected researcher in the whole Hydrogen Program. The project is internally well coordinated and well integrated into the MHCoE. Roles and responsibilities are clearly established. One does have to wonder how the 16 partners listed on slide 2 actually participate on a year-to-year basis, but slides 23 and 24 do clarify the importance of collaboration in this project.
- The collaboration is visible.
- The project has excellent and broad collaborations both nationally and internationally.
- The many and excellent collaborations within this project have been the key to its relatively good value.
- Very strong examples of collaboration spanning industry, academia, and even with international entities. The project clearly leverages external analysis techniques and also serves as a resource to others.

Question 5: Approach to and relevance of proposed future research

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

- The project is in its final stages. There are limited opportunities to do major work.
- Reviewer suggests that added aluminum be tried with lithium aluminum hydrides.
- The future plans do build on past progress and still clearly address overcoming barriers. But it is unclear what will happen to the work on the nano-confinement of magnesium and aluminum hydrides. It seems that only the borohydride cycling studies and the hydrogenation in non-conventional solvents work will continue. Perhaps knowing what the budget for this project will be in 2011 and beyond would answer this question.
- It is necessary to refine the well-to-tank analysis for lithium aluminum hydride recharge in solvent by Argonne National Laboratory especially given that this system is included in the engineering CoE plan. For example, it is proposed that the cyclic stability is included in these calculations as the results become available experimentally; i.e., recycling of the titanium-aluminum.
- In the short time remaining, future plans look fully adequate.
- Given the impending end of this project, the cited future work is about as good as one can do.
- Mapping of all the materials studied on the DOE weight-volume plot would be useful in the final report. Include both theoretical capacity and actual reversible capacities achieved.
- Future work is a logical extension of current progress in each area. For borohydrides, focus is on optimizing reversibility and understanding tradeoffs. The regeneration work on lithium aluminum hydride shows that this project is focused on the practical aspects of implementing this material.

Strengths and weaknesses

Strengths

- There are strong chemistry underpinnings that drive the work.
- The team is experienced.
- Unique approaches are employed.
- Concern for cost is a background to choices.
- The project incorporates a knowledgeable and dedicated PI, a broad-based team of collaborators, and lots of experience with what won't work in the realm of on-board hydrogen storage.
- Worldwide collaboration and very good progress.
- The project explored numerous promising hydrides. Many potentially useful systems have been identified.
- Good, innovative chemistry.
- Ability to change directions as needed.
- Extraordinary collaborations.
- Very competent group focused on the fundamental challenges with metal hydrides; e.g., kinetics and off-board regeneration).

Weaknesses

- None are obvious.
- In the past, the scope was too broad at times.
- None significant at this late stage.

- Project scope is a bit scattered, but it technically is demonstrating success in each area.

Specific recommendations and additions or deletions to the work scope

- Again, reviewer suggests that added aluminum be tried with higher titanium loading in the lithium aluminum hydride work.
- Good to see super critical carbon dioxide out of the picture. IThis reviewer felt it never had a chance of working from day one.

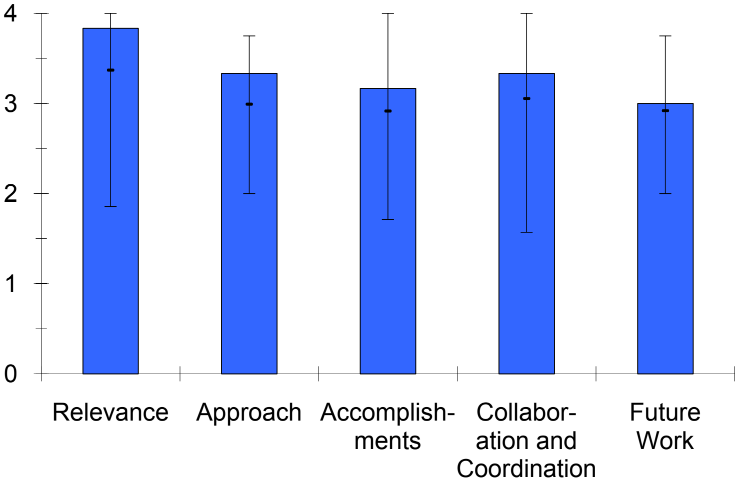
Project # ST-32: Lightweight Metal Hydrides for Hydrogen Storage

J.-C. Zhao; Ohio State University

Brief Summary of Project

The overall objective of this project is to discover and develop a high capacity (> 6 wt%) lightweight hydride capable of meeting or exceeding the 2015 DOE FreedomCAR and Fuel Partnership targets. Objectives for fiscal year 2009 were to: 1) study magnesium borohydride, especially by synthesizing and studying the stability of magnesium dodecaborate (an anhydrous compound not obtained), and 2) study aluminoborane compounds AlB_4H_{11}, AlB_5H_{12} and $AlB_6H_{13}$for suitability for hydrogen storage. Objectives for fiscal year 2010 are to: 1) study the absorption and desorption kinetics with and without catalysts to improve the reversibility of AlB_4H_{11},and other aluminoborane compounds, and 2) study their structures and kinetic mechanisms.

Overall Project Score: 3.3 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.8** for its relevance to DOE objectives.

- With a sharper focus on high capacity reversible material development, this project is now the only major experimental project left in the metal hydride (MH) field.
- This project is well aligned with the Hydrogen Program and DOE research, development & demonstration (RD&D) goals and objectives. The work of this project directly explores materials that have the potential to meet the DOE 2015 hydrogen storage targets. Research is focused in part on selected aluminoboranes that have actually passed a recent go/no-go assessment.
- The project is relevant to the mission of the DOE Hydrogen Program. It addresses lightweight borohydrides.
- As part of the MH Center of Excellence (MHCoE), the project is well aligned with the overall objective of the CoE and Hydrogen Program. It aims to discover and synthesize novel, lightweight materials to meet DOE targets.
- The project aims to achieve some critical DOE targets, in particular gravimetric hydrogen-density and reversibility. Some additional information on the volumetric density of the developed materials would have been useful.
- The project is clearly focused on the rapid discovery of new metal hydrides and definitely supports the DOE RD&D plan.

Question 2: Approach to performing the research and development

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

- There is subtle but important focus on high potential material candidates. It is recommended that this project augment their work with an ongoing theoretical project, specifically ST028 (Wolverton).
- The approach does address technical barriers in an appropriate manner; the project appears to be well designed, feasible, and integrated with other efforts within the MHCoE. Is it possible that some of the unanswered questions (like the structure of AlB_4H_{11} and the "yellow" material) could be resolved by electronic structure type computational methods? Application of methods like energy dispersive spectroscopy or electron microscopy might also add useful characterization information.

- The project's approach is sound with the specific goal on synthesis of new AlB_xH_y complex materials. The project appears to be well structured and focused on a systematic approach to synthesis and characterization of new materials.
- For each new material under consideration, the PI should carry out a quick assessment of the thermodynamic limitations of material regeneration before spending too much effort on hydrogenation.
- Based on some old unappreciated literature, the project has nicely moved into some interesting aluminoboranes. These materials are not being studied anywhere else within the DOE program and offer new opportunities.
- The effort consists of complimentary synthesis, pressure-composition isotherms , and numerous other characterization techniques.
- The work is a bit scattered and haphazard at times, but still seems to move nicely.
- The approach for the project that was given was specific for this year (on aluminoborane compounds), unless some sort of up selection of these compounds was performed. Some level of continued materials discovery of new compounds is encouraged but should be balanced with the focus on particular promising compounds as is done here; i.e., should be balanced.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- The research team has indeed made some significant progress toward meeting goals and accomplishing objectives and has produced some evidence of success in overcoming one or more barriers to on-board hydrogen storage. Key examples are listed below:
  - AlB_4H_{11} showed reversibility under mild conditions; endothermic desorption and thermodynamic reversibility also observed.
  - Cycling AlB_4H_{11} didn't change apparent amorphous structure; i.e., no formation of borides that would be hard to reverse.
  - Synthesis of new phases continues; one new phase is undergoing characterization.
- This reviewer would be inclined to give a higher rating when the "unknown" structures have been worked out and the performance characteristics fully evaluated.
- Identified a pathway to synthesis of AlB_4H_{11}. Showed some reversibility.
- Prepared a new aluminoborane with unknown structure.
- Significant findings made in synthesis of the new AlB_4H_{11} and its derivatives.
- The various aluminoboranes are showing good gravimetric capacity, rather low desorption temperatures, and in some cases partial reversibility (AlB_4H_{11}).
- Overall, the results are many and promising from thermodynamic and kinetic perspectives.
- One shortcoming is significant diborane in the diatomic hydrogen released. It needs to be determined with further mechanistic studies, if there are hopes of reducing the desorbed diborane to acceptable levels.
- The recent work on ammonium-substituted borohydrides offers new possibilities. Ammonia contamination of the diatomic hydrogen will offer challenges.
- This reviewer would have liked the progress report to have included some volumetric capacity calculations to help judge if these new materials will likely meet that DOE target. (During the question and answer part of the presentation, the PI answered this question positively. The high volumetric hydrogen densities of these materials should be included in the final report).
- The technical progress is always very strong for this project. It is clear the PI is very focused on hydrogen storage and is capable of rapidly synthesizing and characterizing new metal hydrides. The compounds that are being explored are out-of-the-box concepts and not being pursued in other projects. The progress on AlB_4H_{11} is thorough and promising with a detailed level of understanding.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- It is recommended that this project augment their work with an ongoing theoretical project, specifically ST028 (Wolverton).

- The collaboration/partnering in this project seems for the most part to be appropriate, well organized, and properly coordinated. It is possible that some additional expertise in areas like molecular structure calculations, other types of spectroscopy; e.g., Raman spectroscopy, electron spectroscopy, and/or electron microscopy, might help answer lingering questions about compositions and structures.
- The project is part of the MH CoE and appears to be well connected to other contributors and resources; however, it was not clear from the slides and presentation what the roles of others are, and especially what results came from where, and etc.
- Collaborations are excellent.
- Many good national and international publications and presentations.
- The project is highly collaborative, leveraging external resources for characterization with partners such as the California Institute of Technology (Caltech), the Jet Propulsion Laboratory (JPL), etc., and synthesis knowledge with partners like the Oak Ridge National Laboratory (ORNL).

Question 5: Approach to and relevance of proposed future research

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

- The future plans do build on past progress and are generally focused on overcoming barriers to on-board hydrogen storage. However, these plans are stated in a rather general way that has a "more of the same" tone to it. This reviewer would like to see some quantitative performance targets for future results spelled out so that one can better gauge future progress.
- Description of future work is somewhat vague and need to be more specific.
- Future plans sound good.
- There is a need to realize the difficulty of gaining mechanistic understanding of reversibility due to the amorphous nature of these aluminoboranes.
- The approach is good, given the limited time left for this project.
- Work is a logical extension of current progress, however a question is if they intend to stick with aluminoboranes or continue with a more broad materials discovery effort.

Strengths and weaknesses

Strengths

- Strong synthesis background.
- The project is working on a class of materials that does have a chance of meeting DOE RD&D performance targets for on-board hydrogen storage, is staffed by a team of knowledgeable scientists, and high hydrogen content materials are being considered.
- The project has strong synthesis capabilities.
- Good chemistry and materials science knowledge and experience is being used in this project.
- The project uses different materials from most other DOE projects.
- Very strong synthesis and characterization expertise is being used in this project.

Weaknesses

- The project may be missing out on useful input from some informative characterization methods that are not currently part of the project. Consideration needs to be given to the question: what are the most informative ways of elucidating the composition and structure of amorphous materials. It is not clear whether reversibility will be achieved.
- As a result of the nature of this particular class of materials, the research is very fundamental and the probability of finding a successful storage material is, unfortunately, very low.
- No substantial weaknesses.

Specific recommendations and additions or deletions to the work scope

- The project will benefit from the PIs developing a more organic working relationship with a theoretical project within the hydrogen program.

- One of the interesting features of the work going on in this project right now is that they are running into amorphous materials with encouraging performance properties. This poses the question if amorphous state of matter the way to go for high capacity, easily reversible hydrogen storage.
- Highly recommend the project adequately address the following non-trivial issues and potential show-stoppers for each newly synthesized material as early as possible: the degree of reversibility, safety, synthesis reproducibility, material purity, charging/recharging kinetics, synthesis, complexity, yield and cost. This reviewer would include a little calculational work on volume to better show the potential advantages of the aluminoboranes.

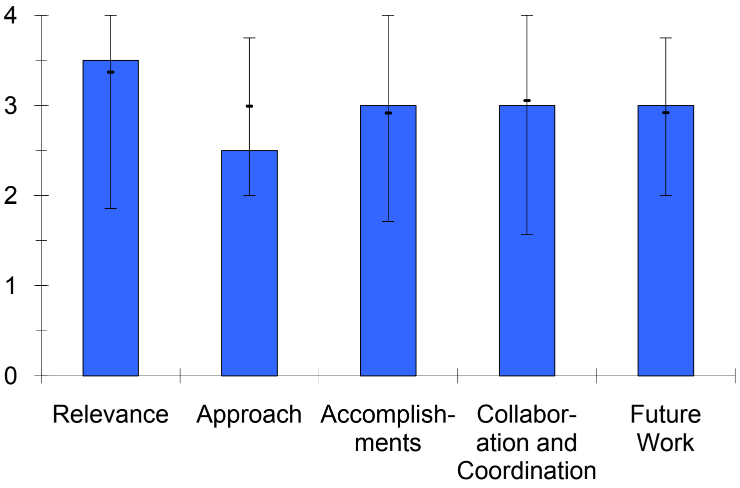
Project # ST-38: Hydrogen Storage by Novel CBN Heterocycle Materials

Shih-Yuan Liu; University of Oregon

Brief Summary of Project

Objectives for this project are to: 1) focus on cyclic diatomic hydrogen storage materials containing carbon, boron, and nitrogen; 2) investigate a new approach to diatomic hydrogen storage that complements the materials currently under investigation; 3) couple exothermic diatomic hydrogen desorption from boron-nitrogen with endothermic diatomic hydrogen desorption from coated carbon (CC) in a cyclic system to address reversibility for on-board hydrogen recharge; and 4) foster a strong collaborative effort with feedback loops between theory, synthesis, catalysis, and charge/discharge characteristics measurements.

Overall Project Score: 3.0 (4 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- The project supports the Hydrogen Program's goals and objectives. It may generate a number of novel materials for hydrogen storage applications.
- The project is aimed at achieving some key goals: capacity and low spent fuel recharge energy.
- Generally high, although near-term original equipment manufacturers (OEMs) will not likely use off-board chemical hydride systems.

Question 2: Approach to performing the research and development

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

- The approach is similar to that proposed by other researchers working on hydrogen storage in organic materials. However, in this case, the research objectives are quite different.
- Making lower free energy of reaction (ΔG) materials with reasonable capacity is a good route.
- Theory guide to synthesis is a good idea and a good approach.
- Finding a combined endothermic/exothermic materials system that yields a slightly endothermic net reaction for automotive use is an interesting and valuable approach. However, the materials proposed are overly endothermic to release the diatomic hydrogen off with >100kilajoules per mole (kJ/Mol) and overly exothermic with >100kj/mol for spent fuel regeneration.
- Also, 25+kcal for the enthalpy of reaction (ΔH) is terribly unrealistic – nearly helf the energy stored in the hydrogen is consumed. Also, the material is currently not liquid over enough of the temperature range.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Progress has been outstanding considering the limited funds.
- Very interesting chemistry is used.

- Materials developed may have applications in a variety of areas adjacent to hydrogen storage, for example, non-conventional fuel cells.
- Overall, it is a very good project; however, the progress made is a bit slow for 1.5 years at $400,000 per year.
- The project did find a reversal path, but the yield may not suffice.
- The synthesis path is not good enough, and they know this.
- A higher percentage of hydrogen material with a methyl group was made, but there was no data on how it works.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- Tom Autrey and Dave Dixon are the appropriate partners for this effort; the collaboration with D. Dixon at Alabama appears to be of value.
- This project would benefit if it could continue to be part of a materials CoE in the future. This is difficult chemistry—it seems unlikely that one PI can take on all of the tasks necessary to complete this project.
- Current collaboration is reasonably good. However, I would recommend involving an industrial partner.
- Seems like collaboration with the CoE was helpful.

Question 5: Approach to and relevance of proposed future research

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

- Liquefying the materials at subambient temperatures will be critical in making this a useful material for automotive purposes. The liquefying additives must not reduce the material capacity significantly since the starting material is only in the ~7% range.
- My impression is that the PI intends to do direct rehydrogenation on board. Both the hydration and rehydration steps are in the 100-150 kj/mol area—is direct hydrogenation really that feasible? This seems more likely to be an off-board material unless the PI can prove that the exothermic reaction worked.
- A basic research component, a new materials discovery effort, could be added to the task list.
- Plans need to be made.

Strengths and weaknesses

Strengths

- It is an interdisciplinary project that combines elements of materials science and organic chemistry. It has good chances for success.
- The project exemplifies and understands the need for liquid form.
- The project will be aimed at higher capacity materials in time.

Weaknesses

- An industrial partner could make valuable contributions to the project by evaluating scalability of the developed materials.
- Energy is unrealistic.
- Not clear if there have been any studies of hydrogen uptake or release for any of these materials. Data of this type do not appear in the presentation slides.

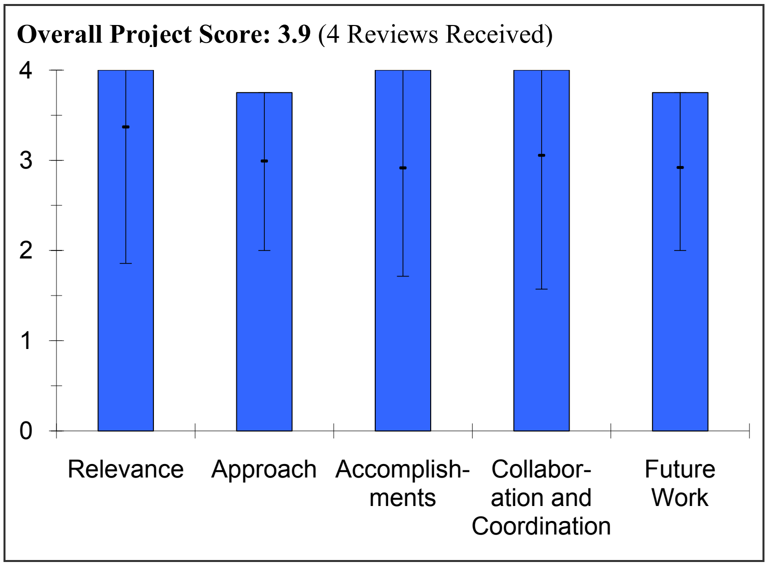
Specific recommendations and additions or deletions to the work scope

- Move to understanding kinetics of release of hydrogen.
- Need to understand if parent can be decomposed without polymerizing to know what the real mass percent is possible.
- Above all, work on a compound that has a ΔH in the 7-12 kcal range.

Project # ST-40: Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Anthony Burrell; Los Alamo National Laboratory

Brief Summary of Project



Objectives for this project are to: 1) complete demonstration of the spent fuel regeneration process and provide data for preliminary cost analysis of the new Los Alamos National Laboratory (LANL) spent fuel regeneration process; 2) develop liquid ammonia borane (AB) fuels and increase the rate and extent of hydrogen release; 3) develop and demonstrate heterogeneous catalysts and continuous flow reactor operation; 4) identify and demonstrate new materials and strategies for near-thermoneutralhydrogen release (with free energy of reaction (ΔG°) = ideally no less negative than approximately -0.8 kcal/mol); and 5) develop materials and processes to minimize gas-phase impurities and demonstrate adequate purity of the hydrogen stream.

Question 1: Relevance to overall DOE objectives

This project earned a score of **4.0** for its relevance to DOE objectives.

- The project aligns with diatomic hydrogen storage objectives. Materials studied have the potential to meet the volumetric and gravimetric targets. The project is focusing on relevant issues, such as impurities generated during hydrogen release and the regeneration of spent AB.
- This project focuses on the efficient release of hydrogen from AB and related compounds and the development of improved strategies for regenerating spent fuel materials. AB and analogs, especially in liquid form, are promising candidates for meeting DOE objectives for a non-reversible, chemical hydrogen storage system. The LANL effort for the optimization of hydrogen release and efficient off-board regeneration of spent AB and related materials is highly relevant and fully supports the DOE objectives.
- The project has definite potential for high levels of hydrogen storage in liquid form.
- Unusually complete consideration of almost all DOE storage objectives: weight, volume, regeneration cost, gaseous impurities, hydrogen release rates, thermal management, etc.

Question 2: Approach to performing the research and development

This project was rated **3.8** on its approach.

- They have been focused on the technical barriers. They have discontinued work in areas such as alkyl ABs to focus on more productive areas. Focus could have been a little more on a cost effective spent fuel regeneration scheme, which is still the main hurdle to overcome.
- A clearly stated and well-formulated approach has been adopted to address the important issues of complete hydrogen release at reduced temperatures and efficient off-board regeneration of spent AB.
- A comprehensive materials development and reaction characterization approach with LANL collaborators is being successfully employed to improve AB hydrogen release properties through addition of ionic liquids and catalysts, and to identify other related compounds; e.g., alkyl-AB mixtures, having potentially improved performance.
- By thoroughly addressing the issues of efficient “one-pot spent fuel regeneration,” fast hydrogen release, and impurity inhibition, LANL has made excellent progress in making liquid AB and related compounds serious

contenders for practical on-board hydrogen storage. Likewise, through their collaboration with The Dow Chemical Company (DOW), a cost analysis is underway to identify all cost-critical spent fuel regeneration pathways and to explore the best ways to reduce system cost.
- Excellent approach for both hydrogen generation and spent fuel regeneration processes.
- The effort was very broad and considered many aspects of AB storage, usage, and spent fuel regeneration; each aspect was studied in substantial detail.
- Excellent combination of AB chemistry and practical experiments. Good engineering orientation.
- Several built-in go/no-go decision points and detailed decision procedures were included in the project approach, which was appropriate.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **4.0** based on accomplishments.

- Excellent work on improving hydrogen release rates using catalysts and ionic liquid additives (collaboration with the University of Pennsylvania (UPenn) and other Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners). Although optimization is still needed, demonstration of an efficient "one-pot" off-board spent fuel regeneration approach is a breakthrough result. This approach is considerably less complex than previous regeneration schemes, and it seems to offer a good pathway for achieving high efficiency regeneration in a high capacity processing environment. Reduction of hydrazine costs seems to be the most serious challenge in the implementation of the LANL regeneration process. However, excellent work is underway to explore cost-reduction options and the development of alternative reactants.
- Good work on cost analysis is being performed by LANL and CHSCoE partners (principally DOW). This is an important component of the project; it is essential to providing a "reality check" at this advanced stage of the project.
- Confirmed the expected copious amounts of impurities (diborane, borazine, and ammonia), but developed a carbon-based adsorbent purification method that will clearly produce pure enough diatomic hydrogen for a proton exchange membrane fuel cell (PEMFC).
- Overall, this project is an exemplary combination of science and engineering that is effectively addressing important issues in the development and deployment of a practical chemical hydrogen storage system.
- The project has demonstrated that the regeneration of spent AB is possible. LANL has devised several regeneration schemes and significantly simplified the regeneration scheme with use of hydrazine and ammonia. This scheme was demonstrated with several different spent fuel forms, which suggests that the technique will work independent of the scheme used to reduce impurities and foaming.
- The metal AB systems and ionic liquids are both very promising.
- The one-pot spent fuel regeneration system is a major improvement that significantly simplifies the AB regeneration.
- Cost of hydrazine for the one-pot regeneration process is an issue for the overall fuel cost.
- A staggering amount of data! Highly productive effort for the level of funding.
- Clearly showed that some forms of AB could be engineered into a vehicular storage system.
- Identified and demonstrated spent fuel regeneration processes, especially the LANL hydrazine process. Showed price of hydrazine has to be lowered before cost target can be met.
- Many other nice details.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **4.0** for technology transfer and collaboration.

- Collaboration within this CoE has been outstanding.
- Excellent cooperation between LANL and CoE partners (especially with UPenn on AB-Il systems and DOW on cost analysis). In addition, LANL and CHSCoE partners have in engaged in fruitful interactions with other Centers (especially the Metal Hydride (MH) CoE and the Engineering CoE). LANL is providing superb leadership and coordination of materials development and off-board spent fuel regeneration work.
- Excellent collaborations.

- One of the best examples of good collaboration within any of the DOE activities.
- Much of the collaborative success comes from the efficient and open operation of the CHSCoE.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.8** for proposed future work.

- Project is ending.
- Good plans are in place to conclude the project and transfer technology to the Engineering CoE. Unfortunately, with the conclusion of the CoE, it is unlikely that the concepts studied thus far will be developed to the extent needed for complete and seamless technology transfer. However, it is hoped that work can continue at even a reduced level on optimization and validation of AB-Il-catalyst systems and on complete, end-to-end demonstration of the one-pot regeneration cycle at reduced cost.
- This project is 100% completed, but the final results are very promising and should be continued if at all possible.
- This evaluation is not fully applicable because the project is imminently ending. However, there are some loose ends that remain.
- PI has convincingly argued to continue long enough to complete the details. This reviewer would agree.

Strengths and weaknesses

Strengths

- Good collaboration between experiment, modelling, and engineering analysis.
- Highly quaiilfied research, development, and engineering team has been assembled at LANL and at collaborating CoE institutions. Focused effort on improvements in hydrogen release in AB, AB derivatives, and related materials is showing considerable promise. Likewise, using well-coordinated efforts to improve spent fuel regeneration processes will complete the overall engineering cycle and bring this technology closer to practicality.
- Extremely strong chemistry approach and team.
- Excellent fundamental science and engineering.
- Very close to meeting DOE targets and practical application.

Weaknesses

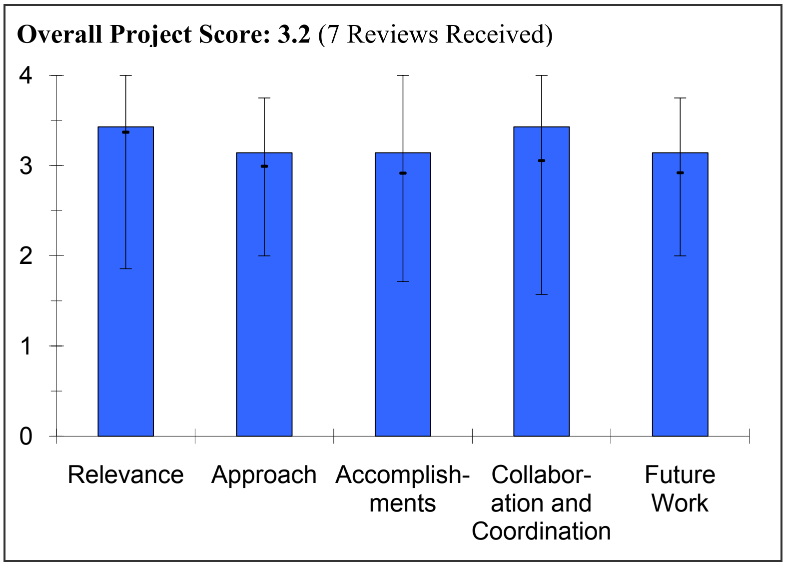
- Project is ending.
- None.

Specific recommendations and additions or deletions to the work scope

- Strongly recommend that DOE find a way to provide continued support for this activity.
- Project should be continued.
- Try to continue (renew) in some limited form.

Project # ST-41: PNNL Progress as Part of the Chemical Hydrogen Storage Center of Excellence

Jamie Holladay; Pacific Northwest National Laboratory



Brief Summary of Project

The objectives of this project are to: 1) develop materials and methods for low temperature release of pure hydrogen from chemical hydrides with potential to achieve DOE targets, 2) demonstrate high efficiency methods for large scale synthesis of chemical hydrogen storage materials, 3) develop high efficiency off-board methods for chemical hydride spent fuel regeneration with potential to achieve DOE targets, and 4) support collaborators through expertise in chemistry and characterization to determine the kinetics and thermodynamics of hydrogen release and regeneration of spent hydrogen-storage materials.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- This broadly based project focuses on critical problems in efficient hydrogen release and off-board regeneration of spent chemical hydrogen storage materials. There is excellent synergy among research, development, and engineering efforts at PNNL and collaborators in the Chemical Hydrogen Storage Center of Excellence (CHSCoE).
- The focused efforts on theory, assessment of material characteristics (mainly ammonia borane (AB) and related compounds) and development of novel, yet straightforward engineering strategies and approaches directly address DOE research, development & demonstration (RD&D) barriers as well as performance and cost targets.
- The project is part of the CHSCoE and is well aligned with the objectives of the CoE, namely to develop materials and processes for low temperature release of hydrogen that can meet DOE targets.
- Specifically, the project appears to aim for large scale synthesis of AB and the regeneration of the thermodynamically difficult spent fuel from AB storage material.
- Aimed at higher capacity and efficient recycling with low impurities.
- Mostly aligns with DOE goals and targets. The Pacific Northwest National Laboratory (PNNL) is studying some materials that do not have the potential to meet storage goals—new metal amido borane does not meet the 6 wt% goal.
- Materials are not ready for commercialization, but they do show interesting properties.
- Solid AB has a very high hydrogen storage capacity.

Question 2: Approach to performing the research and development

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

- The project is keenly focused on the technical barriers associated with successful deployment of an AB-based storage system. A methodical and systematic approach has been employed to address vital research and engineering issues, including: 1) elucidation of mechanisms of hydrogen release from AB, 2) development of practical methods to achieve rapid and efficient hydrogen release, 3) reduction of impurities that deleteriously affect system performance, and 4) demonstration of innovative methods for first-fill and off-board regeneration of spent fuel.

- The approach on solid AB and derivatives is complementary to the LANL effort on liquid AB systems. The approaches adopted in these two large R&D activities plus directed efforts in CHSCoE partner institutions are well coordinated and comprehensively address the important barriers associated with this promising system from both on-board and off-board perspectives.
- The project incorporated a theory/calculation-guided experiment approach, deep exploration of the details of reaction, and process reaction engineering, which was helpful.
- Metal amidoborane (MAB) spent fuel regeneration seems unlikely, but may be possible.
- Work is appropriately focused on the technical barrieres of reducing impurities and on spent fuel regeneration.
- There is a good mixture of theory and experiment.
- The CoE eliminated non-competitive materials.
- Solid AB has issues with borazine and ammonia impurity generation along with the hydrogen.
- Solids handling may be problemmatic for vehicular applications.
- The approach of the scale up synthesis of the material appears sound.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- There has been approximately $2 million spent for the following results:
  - Worked down cost of first fill AB production from basic materials to $9/ kg. In part, by redesigning to a flow process.
  - Showed metal changes the reaction path of AB greatly, offering a new route with possible avoidance of impurity streams such as the borohydride, B6H6. However, it does make ammonia at 10 times.
  - Undisclosed endothermic MAB (2 kilocalories (kcal) and 85°C release).
  - Complete boron recovery in plain AB spent fuel regeneration scheme.
  - Progress was made but not completed on low cost route for spent fuel regeneration.
- The project has shown progress in reducing impurities through catalysis, but borazine release was still high from AB; the project has also demonstrated high boron recovery during AB spent fuel digestion.
- Important new results were produced in 2010 on: 1) impurity identification and mitgation in AB dehydrogenation reactions, 2) characterization of AB-metal hydride mixtures which show decreased impurity levels and less foaming than AB alone, and 3) demonstration of a new ammonia synthesis route for more efficient AB first-fill and AB spent fuel regeneration. Also, intriguing new results on characteristics and mechanism(s) of hydrogen release and impurity from metal amidoborones were produced.
- Borazine and ammonia release from AB and metal-amidoboranes remains a problematic issue. However, good results were obtained in 2010 on mitigation strategies involving additives/catalysts to facilitate reduction of impurity concentrations.
- In the metal-AB (M-AB) work, the efficient regeneration of M-AB from spent fuel by simply separating the metal in a conventional AB spent fuel regeneration cycle remains a serious outstanding challenge. At this stage of the project, solid plans should be in place to facilitate metal-AB spent fuel regeneration; e.g., can a variant of the hydrazine-mediated approach adopted by LANL be used?
- One overarching issue is that solid systems are generally not as desirable as liquids for fuel transport and handling in the reaction system. A more detailed examination of approaches for efficient use of solid fuels is needed.
- The team has done a good job addressing issues affecting AB systems; however, many problems remain.
- Significant progress has been made in fiscal year 2010.
- New endothermic proprietary MAB material is a significant development, albeit the hydrogen capacity is below 6 wt%.
- New steps were identified to lower the cost of solid AB.
- The moderately high volume synthesis of the M-AB storage material (even at the 20-gram level) is significant.
- Given the inherent huge spent fuel regeneration challenge of these chemical hydrides, the project results are significant.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- There was a good number of very useful collaborations.
- There are good collaborations, both within the CoE and with outside institutions.
- The PNNL technical efforts are enhanced by extensive and fruitful collaborations with CoE partners and external institutions. There is a good division of effort and the R&D effort is well managed and coordinated.
- Good work was accomplished with CoE partners.
- The CoE "Lessons Learned" slide indicates that trust between some of the CoE partners (unidentified) was a problem.
- The project appears to have plenty of collaborative opportunities; however, I assume that managing the high number (15) of institutions may have been a challenge and may not have been as effective as having less partners would have been.

Question 5: Approach to and relevance of proposed future research

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

- This project is 95% complete—the future plans are not commensurate with that timeline; however, they do suggest remaining work that would be needed if CoE activities would continue.
- Time seems insufficient, but they have a good plan.
- Although the work on hydrogen release from M-AB compounds is interesting and potentially important, very little attention is given to the important issue of M-AB spent fuel regeneration.
- Approaches and concepts for efficient distribution and handling of solid fuels are needed.
- Not applicable. The CoE closed.
- The project is ending, this project is essentially over.

Strengths and weaknesses

Strengths

- Highly quailified research, development, and engineering team has been assembled at PNNL and at collaborating CoE institutions. Focused effort on improvements in hydrogen release from AB, AB derivatives, and related materials is showing considerable promise. Likewise, well-coordinated efforts for improving spent fuel regeneration processes are completing the overall engineering cycle and are bringing this technology closer to practicality.
- Includes mix of theory and experiment.
- High hydrogen capacity and simplicity of solid AB.
- The demonstration of high volume synthesis of AB is significant.
- The down selection of materials shown in the summary table for diatomic hydrogen is useful.
- PNNL continues to set the bar very high. Overall, they have done an excellent job with the Chemical Hydrogen Storage CoE.

Weaknesses

- Insufficient emphasis on M-AB spent fuel regeneration and concepts for distribution and handling of solid fuels.
- Impurity and rate issues with hydrogen release.
- The difficult nature of the chemical hydride materials.

Specific recommendations and additions or deletions to the work scope

- Some formalized method to hand things off to the Engineering CoE would be beneficial—overlap or transfer of some staff would be the most efficient way.

- The researchers should take a closer look at efficient M-AB spent fuel regeneration schemes and effective methods for solid fuel handling and distribution.
- Reviewer recommends that DOE find a way to provide continued support for this activity.
- The project team should address the presence of contaminants such as ammonia and borazine quickly, as it can be a show stopper.
- The project team should spend more effort on resolving the spent fuel regeneration issue and not on scale up synthesis.

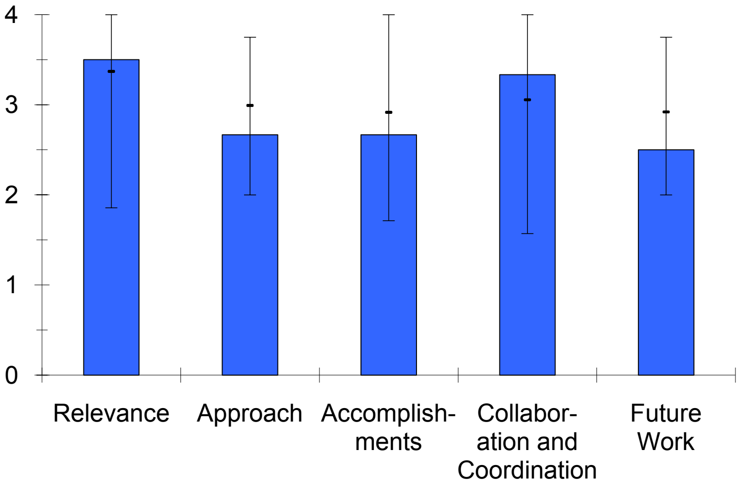
Project # ST-44: SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence: Design and Testing of Metal Hydride and Adsorbent Systems

Ted Motyka; Savannah River National Laboratory

Brief Summary of Project

Objectives for this project are to: 1) collect and assimilate property data for metal hydrides and adsorbents, 2) collect operational data for storage vessel configurations, 3) develop general format for models, 4) assemble and test models, and 5) develop an "acceptability envelope" of media characteristics based on 2010 and 2015 DOE technical targets.

Overall Project Score: 2.9 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Generally high—a systems-level understanding is required to understand how to build an automotive grade tank.
- This project meets the target of DOE.
- This project is consistent with the objectives of the Hydrogen Program and fully supports DOE research, development & demonstration (RD&D) objectives.
- All project aspects align with the Hydrogen Program and DOE RD&D objectives. However, in order to give an "outstanding" rating, I would have to assume that parallel considerations for chemical hydrides are covered in another part of the Hydrogen Storage Engineering Center of Excellence (Engineering CoE) (which it turns out they are).
- Project approach is designed to achieve the ultimate goal of the Engineering CoE.
- This is an exercise in futility since no viable metal hydride or otherwise hydrogen storage material capable of meeting the DOE diatomic hydrogen storage material targets for on-board vehicular use is available. It is, therefore, unclear why this activity should continue. DOE dollars would have been better spent on funding smaller projects that research new hydrogen storage material concepts.

Question 2: Approach to performing the research and development

This project was rated **2.7** on its approach.

- Good to introduce novel concepts—what about integrated concepts like the aluminum mesh being used by Van Hassel's group (project ST-006)? Such concepts serve as both heat transfer mediums and material stabilizers.
- The size of the tank is unclear in the model, for instance is it only for 100g or a larger 5- to 6-kg tank, or is it 1 kg as some slides indicate. How will they predict the performance of a full scale system was not clearly explained nor how they validate the model if the CoE doesn't construct a bigger system.
- The model of thermal management seems to be investigated. However, real hydrogen storage tanks using hydrogen storage materials have various issues including expansion and contraction of materials with hydrogenation and dehydrogenation, swelling of materials, the amount of powder in the vessel, and so on. This project excludes these significantly important issues from modeling.
- Selection of near- and mid-term metal hydride (MH) candidates for engineering development is sound.
- Compiling metal and adsorption hydride date is critical to modeling efforts.
- Developing an "acceptability envelope" of hydride properties provides a great pathway for the downselection of materials.

- The approach is generally good. I like the "acceptability envelope" aspect of this project, but this type of overall performance analysis should be applied uniformly to all of the storage concepts under consideration by the Engineering CoE, i.e., will the Pacific Northwest National Laboratory (PNNL) and the Los Alamos National Laboratory (LANL) be using the same approach for chemical hydrides.
- There is no detailed schedule given that would enable one to gauge at what point in the program plan model validation would start.
- The PI's approach lacks the core premise of having a viable hydrogen storage material available. Without that, the sophisticated engineering analysis, model building, CFD work, etc., is unlikely to produce a viable system-level hydrogen storage tank to DOE specifications. Why is it a good idea to model an activated carbon (AX-21) or metal-organic framework- (MOF-5) when if they are not going to deliver at system level if they fail at the material level.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- Good.
- At present, only methodologies were shown.
- Resources devoted to sodium aluminum hydride may be wasted since sodium aluminum hydride has no chance of becoming a viable diatomic hydrogen carrier due to very low system capacities that will not meet DOE targets.
- Development of the kinetics, heat, and mass transfer models are on target.
- If the numbers were understood correctly, well over a million dollars has been expended on this work since the start of the project. The accomplishments from this work are mainly: 1) the gathering, evaluation, interpretation, and assimilation of data into models; 2) the development and application of the "acceptability envelope" to metal hydrides; 3) the development of a model for adsorbents; 4) the validation and testing of the metal hydride models; and 5) the development of optimization studies of the vessel configuration for sodium aluminum hydride. Much of what was presented was called "baseline" analysis. Hopefully there will be much more to show for this kind of funding expenditure in future years, including some concrete technical findings that push prototype system development work in the right direction.
- Progress on technical accomplishments appears to be on track; however, no detailed schedule was provided. The "refined" model for a physisorption storage system needs further improvement when compared with the measured thermal profiles.
- Having stored (or aiming to store) 1 kg of hydrogen in 12 minutes is not really an accomplishment. Progress has been minimal. PIs have too much on their plate.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- Good.
- The project contains some distinguished experts of the field, but others are missing that should be included.
- Excellent collaborations among the many CoE partners.
- Appropriate, well integrated, and seemingly effective collaborations with other institutions; partners appear to be full participants and are well coordinated within the various tasks.
- Very strong team established.
- There are many entities involved–perhaps too many. It is not made clear how closely these groups work together. No example of close collaboration that resulted in a tangible improvement was given.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- This effort is part of the CoE and includes working with original equipment manufacturers (OEMs).

- The issues that have been mentioned in the "technical accomplishments" section should be investigated. For that purpose, construction and testing of prototype tanks should start very soon.
- Proposed future work is very good.
- The future plans read like more of the same in terms of approach and emphasis. This reviewer doesn't have a warm, fuzzy feeling about bang for the buck where this project is concerned. The participants in this project should work toward a strong showing in 2011 by deeply engaging the issues to produce concrete go/no-go recommendations for future technical developments—baselining isn't going to be enough.
- Need to establish a clearly defined test matrix of candidate storage materials.
- Building hardware and software models around MOF-5 and MaxSorb as the hydrogen storage materials appears to be an academic exercise. It is unclear how this activity can result in an acceptable system-level hydrogen storage tank because they are starting from a storage compounds that do not meet DOE's programmatic goals for on-board diatomic hydrogen storage.

Strengths and weaknesses

Strengths

- Modeling of thermal properties with candidate materials are under way with collaboration of excellent experts.
- There is strong collaboration.
- The partners have excellent understanding of the technical work.
- The project is well organized.
- The project has a well defined architecture in the modeling hierarchy toward addressing the Engineering CoE goals.
- There is a very strong team contributing to the project.
- Successful completion of model development will establish the theoretical boundaries of expected performance from any given storage system design and storage media.
- Researchers and scientists involved in this Engineering CoE are capable individuals with resources available to them.

Weaknesses

- Only thermal properties, such as thermal conductivity, is taken into the consideration. However, there are a numbers of issues to be considered to design tanks utilizing hydrogen storage materials.
- None.
- The project is looking only to "preliminary prototype designs" by the end of Phase I. I would like to see an emphasis on results that are more substantive than just "preliminary".
- Project activities have a high potential for replication of effort, past and present.
- While no detailed schedule of project tasks was given, the success of the project is likely to be constrained by time unless media property data become available very early in the project schedule.
- Software models and hardware designs are based on a yet-to-be-discovered hydrogen storage material with unknown characteristics and thermophysical properties. The lack of cost considerations is a real issue.

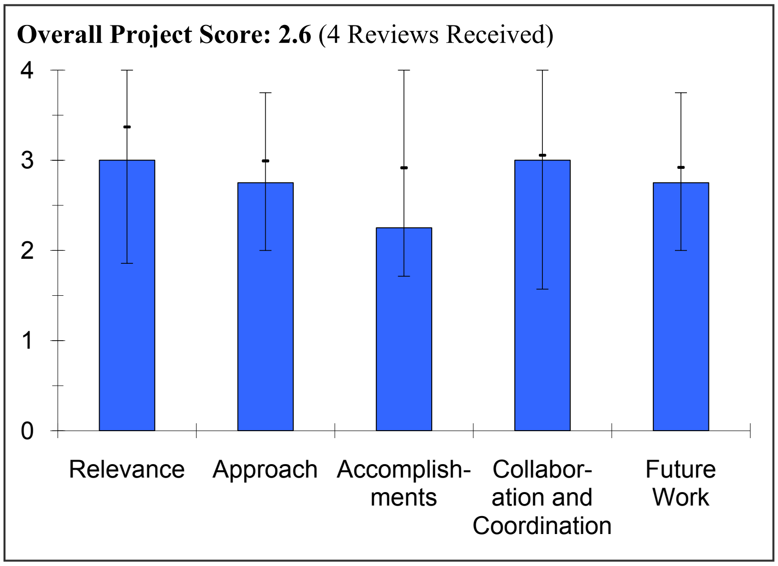
Specific recommendations and additions or deletions to the work scope

- Every factor that influences the tank performance should be investigated. To that purpose, testing with the real tanks is indispensable. The size of a 100-g tank seems to be too small.
- Step up the pace of work—raise the ambition level.
- Prepare a detailed schedule of tasks and milestones.
- Reduce and revise the scope of work.

Project # ST-45: Key Technologies, Thermal Management, and Prototype Testing for Advanced Solid-State Hydrogen Storage Systems

Joseph Reiter; NASA Jet Propulsion Laboratory

Brief Summary of Project



Objectives for this project are to: 1) provide management tasks in support of the Hydrogen Storage Engineering Center of Excellence (Engineering CoE), 2) serve as technology team lead for thermal insulation research and development, 3) perform insulation material testing and validation, and 4) perform metal hydride prototype testing and evaluation. The purpose and focus of the Jet Propulsion Laboratory (JPL) effort is technology management, including: 1) assessment of current state-of-the-art and fitness evaluations of existing technologies; 2) identification of technology gaps in regards to system requirements and operational demands; 3) assessment of impact of technology gaps on system developability; 4) selection of candidate approaches to device design and implementation for gap mitigation; 5) technology development, hardware design and analysis for selected technologies; and 6) continuing assessment and feedback of emerging technologies.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- This project meets the goal of the Hydrogen Project.
- This project is an integral part of the Engineering CoE and is only 20% complete (one year). The tasks to be performed by JPL are relevant to the goals and objectives of the Engieering CoE and, as such, are relevant to the DOE Hydrogen Storage Program. The primary technical contribution will be in the areas of high and low temperature insulation. JPL will also provide "technology management" for CoE activities.
- Heat transfer is a critical parameter for many hydrogen storage systems and with other components of hydrogen fuel cell systems. Having accurate, reliable, and VERY current data on engineering materials should be helpful to the researchers and designers of these systems.
- This project has some specific roles within the Engineering CoE and thus has implicit connection to the DOE goals and objectives.

Question 2: Approach to performing the research and development

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

- There are three tasks in the project, but they are a little bit dispersed.
- JPL will use its extensive experience and background in thermal insulation to contribute to the Engineering CoE objective. The proposed approach building on this capability appears to reasonable and adequate.
- The combination of literature and Internet surveys and future material properties testing should help fill any gaps in the open literature, if there are any.
- Given JPL's long history in practical metal hydride technology devices, its initial activity seems rather limited compared to the overall budget allocated.
- This effort is mainly a management role in the area of "enabling technologies." It manages the cryoadsorbant engineering effort.

- JPL's only technical role, at least in Phase 1, is in the area of "thermal insulation," applicable mainly to cryocontainment.
- Later in Phases 2 and 3, JPL will be involved, more appropriately, in prototype design and construction.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.3** based on accomplishments.

- Task 1 has been completed very quickly.
- Technical accomplishments after the first year (20% complete) of this project appears to be rather limited, involving literature surveys and data base development. Given their experience in similar thermal insulation systems (for space applications), it could be assumed that this data would be readily available at JPL.
- So far, the database is mostly a literature study.
- Accomplishments, so far, have been very limited. Spending has been rather low for the first year. It is not clear if this is a result of DOE interim spending allocations, or the effort is behind schedule.
- The main management effort seems to be not underway yet.
- JPL has appropriately gathered commercial insulation information and provided a useful database for the Engineering CoE (delivered this month).
- Thermal performance is not quite started, but the equipment is nearly in place.
- In spite of the slow start, to quote the PI, "fiscal year (FY) 2010/2011 will be an extremely busy period!" (slide 19).

Question 4: Technology transfer/collaborations with industry, universities, and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- The California Institute of Technology (Caltech) seems to be a major player in this project, and other people strongly support them.
- JPL appears to be collaborating with the other Engineering CoE partners, especially in the system architecture development area.
- Ideally, the matrix nature of the organization is very effective, but there can be breakdowns with slight variations of the normal, especially in communication or availability of resources.
- The Engineering CoE provides nice collaborations. It is not clear from the presentation how well they are working at this early point.

Question 5: Approach to and relevance of proposed future research

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

- FY 10/11 will be very busy. Plan and schedule should be rearranged to average the duties of the project.
- Future work plans seem to be consistent with overall Engineering CoE goals and objectives and with CoE schedule for system design and development.
- Continue as planned within the directives of the Engineering CoE.
- One might question the rather large effort on thermal insulation, being that it is applicable mainly to cryostorage. Is this not being covered partly in the long-standing Lawrence Livermore National Laboratory (LLNL) cryocompression project (ST-03)?
- This effort is apparently what the Engineering CoE needs.

Strengths and weaknesses

Strengths

- Caltech has experience and expertise in testing.
- Extensive experience in thermal management subsystems.
- Experience in technology management and system architecture definition.

- Potentially developing a large data base of thermal properties of relevant materials, combining literature studies with physical measurements.
- Past JPL experience on hydrogen-storage prototype systems.

Weaknesses

- Task 1 and 2 are separate subjects to Task 3.
- None apparent at present.
- It may be difficult to make the materials database more attractive to a researcher/developer than their own literature and Internet search study. The team should work hard to make the database very user friendly, practical, and complete, or this part of the project expense may be negated by hydrogen researchers using the Internet more than this product. Most likely the key element of the database will be the most current materials, which means that updates are critical.
- There are questionable roles in Engineering CoE Phase 1. There is no question about the need for JPL in prototype Phases 2 and 3.

Specific recommendations and additions or deletions to the work scope

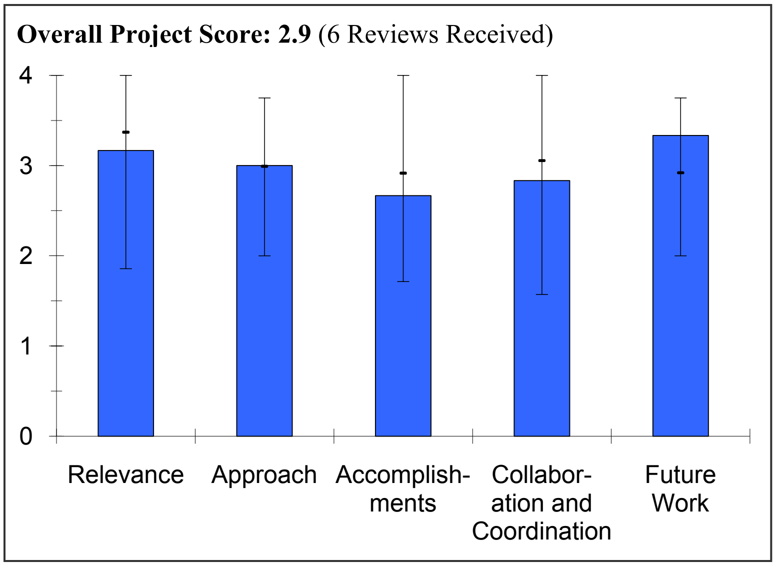
- Good preparation for Task 3 is critical because Task 3 supports the entire project. The success of Engineering CoE depends on the activity of this task.
- JPL should be encouraged to move to the design and testing approaches addressing the specific design requirements for thermal management of the specific systems identified by the Engineering CoE. General testing and "re-validation" of insulations identified in the literature survey should be limited to insulations that can meet the requirements specific storage system designs.
- Since the insulation materials will be used in vehicles, it will be valuable to include the toxicity, respirability, reactivity, and other hazardous characteristics to the database.
- Establish a working relationship with LLNL to make use of their vacuum insulation expertise and experimental cryocontainment activities.

Project # ST-46: Microscale Enhancement of Heat and Mass Transfer for Hydrogen Energy Storage

Kevin Drost; Oregon State University

Brief Summary of Project

The objective for this project is to use microchannel technology to: 1) reduce the size and weight of storage, 2) improve the charging and discharging rates of storage, and 3) reduce size and weight and increase performance of thermal balance of plant components.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- The project addresses the problems of system weight and volume, charging and discharging rates, and thermal balance by applying well-established microchannel technology. In this engineering approach, the use of microchannels addresses the enhancement of heat and mass transfers in storage systems.
- This work is relevant to the Hydrogen Program and DOE research, development & demonstration (RD&D) objectives.
- Microchannel technology has the potential to significantly reduce system weight and volume.
- The project "Microscale Enhancement of Heat and Mass Transfer for Hydrogen Energy Storage" is relevant to Hydrogen Program and supports DOE RD&D objectives. This microchanneling technology may reduce size, weight, and charging time for hydrogen storage.
- Microchannels are useful and can reduce size and weight in certain applications. Microchannels have been oversold in other applications. It is not clear if microchannel geometry will help in these applications where it would be difficult to place the microchannels in the material of interest, and coating the material of interest on a microchannel surface (heat exchanger) could increase the weight.
- The project does properly support DOE goals by attempting to decrease storage weight and volume and increase tank discharge rates by improving heat exchange and internal flow.
- The PI’s description of the rationale and relevance of this activity to the ultimate objectives of the Engineering CoE is clear, succinct, and well established. The only weakness is the lack of attention to cost factor; i.e. how expensive these systems are and how cost consideration would affect the choice and features of the Microtechnology-based Energy and Chemical Systems (MECS) design, etc.

Question 2: Approach to performing the research and development

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

- The approach of the project is to develop models, design and predictively evaluate components, fabricate proof-of-principle test articles, conduct proof-of-principle tests, and use the results to validate the predictive models.
- The approach is well planned in three phases. The project is currently in Phase 1.
- The approach to use microchannel technology to reduce barriers to heat and mass transfer is good. They are focused on optimizing the performance of a single unit cell; i.e., an individual microchannel, and then “number up.”
- The approach taken here “is microchannels are the solution, now look for a problem in the diatomic hydrogen storage Engineering CoE to apply them to.” This is generally not as effective an approach as defining the problem and then looking for an appropriate solution.
- Go/no-go decisions should be based on system requirements.

- It is not clear how the microchannel insert will improve heat transport or diatomic hydrogen transport in the diatomic hydrogen storage tank. For heat transfer, the limiting rate will be the heat transfer between storage material particles. The microchannel does not appear to address this. The poster states that "metal hydride powder will be patterned with micro-channels to investigate effect on diatomic hydrogen gas distribution throughout reaction volume." Decrepitation will degrade the microchannels if they are formed in the powder or pressed storage material. Decrepitation will also make it difficult to control the contact between microchannel plates and the storage materials, which will affect heat transfer.
- The microchannel combuster/heat exchanger seems more promising.
- This project is under the Engineering CoE and will hopefully provide novel heat exchanger designs.
- The approach is to use small channel heat exchangers to improve heat and mass transfer, which is logical.
- The contractor will also attempt to design and build a microchannel combustion unit to preheat oil for the hydride desorption process. This is especially useful for high temperature (high enthalpy of reaction (ΔH)) hydrides where supplementary high grade heat input will be required.
- Intuitively, cost may be a challenge. Manufacturing cost estimates will come later in the project.
- The PI's approach is reasonable, but it does not address the central issue of not having a viable candidate material for hydrogen storage. Also, the approach to dealing with cost issues has not been fully addressed.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- A tank insert integrated diatomic hydrogen distribution and heat exchanger plate was constructed. Calculations of multiphase Navier-Stokes equations for mass and energy transport between gas and hydride phases were performed. Preliminary modeling for combustor with surface reactions is ongoing, with different adsorption, surface, and desorption reactions identified. A lightweight combustion heating system for desorption of hydrogen from metal hydrides was evaluated and found feasible.
- This is a new project. Technical accomplishments are limited by the fact that it is still in an early stage of development.
- The progress was dampened by funding problem but completed the identification of the highest value applications of microchannel-based technology, including completion of design and fabrication of tank insert unit cell test apparatus.
- Reviewer is not sure how the tank insert concept was determined to be the top priority since no modeling was presented to show the potential of microchannels in this concept, such as can it improve things by an order of magnitude, a factor of two, or by 10%. If this work started in February 2009, not much has been accomplished over this time.
- The model validation for pressure drop appears to be a one-point validation—this is inadequate. The project should validate over several flow rates to get the shape of the curve and ensure proper flow rate dependence.
- Hydrogen combustor/heat exchanger work seems more useful since they have provided a quantified weight benefit.
- The project has had a slow start (8% spending in the first 15 month). It is unclear if this a DOE funding delay, or the fault of the contractor. Nonetheless, a number of technical accomplishments are cited. Most seem to be on paper.
- Slide 10 (Technical Accomplishments) states reduced size and weight, and improved rate for both the tank and combustor, however it is unclear if these results are experimental or calculations. In either case, the results are not given or obvious if they are new results or reiterations of the proposal hopes Or if they are the calculation results of the General Motors (GM) study (slide 22).
- The reactor test cell (slide 13) is interesting and innovative.
- The modeling work seems to be going well.
- It is unclear from the accomplishment slide 21 if the experimental facility is in place, or just designed.
- The PI has carried out a considerable amount of good work that, in general, is of value to many applications including hydrogen sorption devices. The work on the MECS-based tank insert, MECS-based integrated combustor/heat exchanger, and the lightweight microchannel combustion system is invaluable and holds great promise.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.8** for technology transfer and collaboration.

- There is an extensive list of partners and collaborators, which includes national laboratories and major U.S. automobile manufacturers, and members of the Engineering CoE team.
- Work is done solely by Oregon State University (OSU).
- The project needs more collaborations with members of the Engineering CoE team in terms of selection of materials for hydrogen storage.
- Collaborations appear to be in place within the Engineering CoE.
- The collaborations within the Engineering CoE are good, at least on paper, but it is unclear if they are working well.
- The GM collaboration looks like a good example.
- Good collaboration with other team members is clearly evident.

Question 5: Approach to and relevance of proposed future research

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

- The proposed future work is mostly focused on completion of different tasks, such as simulation of optimized tank insert and integrated combustor/heat exchanger (µCHX) unit cell, as well as experimental validations.
- The proposed future work is sound.
- The proposed future work related to the complete simulation and testing of the tank insert unit cell including complete design, manufacturing cost estimate for tank insert, and complete design and testing of the microchannel heat exchanger are good based on past progress.
- Proposed future work addresses appropriate issues.
- Plans seem logical and fit well with Engineering CoE needs.
- Proposed future work is well described and logical.

Strengths and weaknesses

Strengths

- The project tries a new engineering approach to improve performance of a system, with an anticipated reduction in the size and weight of storage and improved charging and discharging rates.
- The PI has excellent experience with microchannel technology.
- The Microproducts Breakthrough Institute (MBI), a unique product development laboratory operated by OSU and the Pacific Northwest National Laboratory (PNNL) is well suited for the proposed work. The PI brings more than 15 years of experience to this project.
- The project has an innovative heat and mass transfer approach that needs to succeed in order to reach the refueling target time.
- The OSU team is well versed and fully equipped to carry out the work delegated to them by the Engineering CoE.
- The project's engineering technology and theoretical modeling seems to be already in place.

Weaknesses

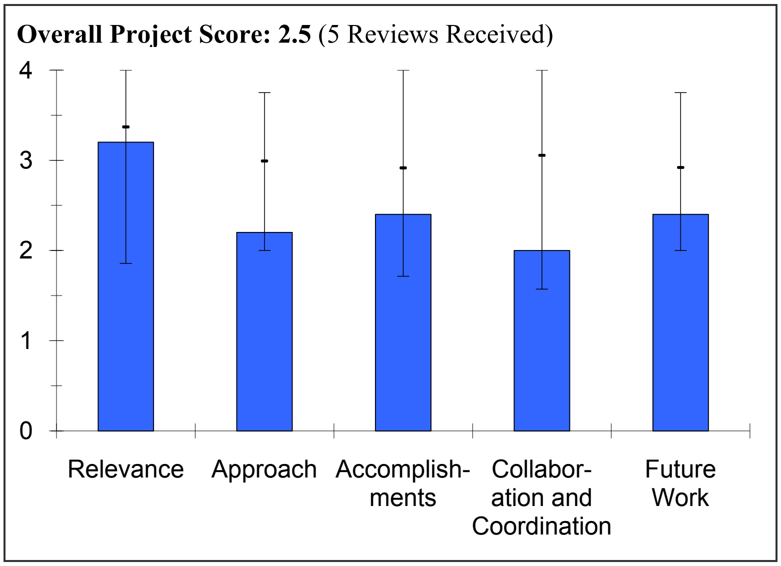
- There is no external collaboration.
- The corrosion issue related to materials of microchannel by hydrogen storage materials is weak.
- The approach is "a solution looking for a problem."
- The concept looks expensive.
- No cost considerations were included.
- Strategies for dealing with hydrogen storage material containment; i.e., problems such as expansion and contraction, decrepitation, etc., are lacking.

Specific recommendations and additions or deletions to the work scope

- The project team needs to do a better job of showing details of potential for microchannel technology to help specific problems in a storage device. How much will it enhance heat transfer? How much smaller or lighter can the heat exchanger be? Modeling should be able to provide some estimates.
- Get manufacturing cost estimates soon.
- Add cost considerations and materials containment issues to the scope of work.

Project # ST-47: Development of Improved Composite Pressure Vessels for Hydrogen Storage

Norman Newhouse; Lincoln Composites



Brief Summary of Project

The objectives for this project are to: 1) meet DOE 2010 and 2015 hydrogen storage goals for the storage system by identifying appropriate materials and design approaches for the composite container; 2) maintain durability, operability, and safety characteristics that already meet DOE guidelines for 2010 and 2015; 3) work with Hydrogen Storage Engineering Center of Excellence (Engineering CoE) partners to identify pressure vessel characteristics and opportunities for performance improvement; and 4) develop high pressure tanks as required to enable hybrid tank approaches to meet weight and volume goals and to allow metal hydrides with slow charging kinetics to meet charging goals.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- High-pressure tanks that are cheaper are critical to the success of the FreedomCAR Partnership goals.
- The project relates to development of improved composite pressure vessels for hydrogen storage, which is essential to the Hydrogen Program, but this project is dependent on what material one uses, and, as such, needs close coordination with the hydrogen storage material's developer. The coordination seems lacking.
- This project is very relevant to the DOE program objectives. Lincoln Composites brings a great deal of experience to the Engineering CoE. A pressure vessel will be required for materials-based systems.
- Storage costs are an important element with respect to enabling cost effective on-board hydrogen storage and therefore hydrogen vehicles.
- This is yet another exercise in futility since no tank-worthy hydrogen storage material that meets DOE hydrogen storage material targets for on-board use is available. It is, therefore, unclear why this activity is needed or should even continue. Again, the most important parameter, cost, has been mysteriously left out of the equation.

Question 2: Approach to performing the research and development

This project was rated **2.2** on its approach.

- The approach is unclear. The PI did not clearly indicate what the primary driver of the project was (cost, safety, weight, etc.). Only after much interrogation was cost revealed as the primary driver. It is clear that the improvements will only be incremental in nature and will not achieve the team's overall targets.
- Project targets are unclear—the PI simply highlights team targets, which, we all know, compressed tanks will not achieve. The PI needs interim milestones and targets to highlight what incremental improvements for which he is aiming.
- There needs to be clarification of what the materials are.
- The approach to performing the work is well designed and the technical barriers are addressed, but integration with other efforts needs improvement.
- The approach is to establish a baseline tank design, evaluate potential improvements, evaluate design concepts, and project the ability to meet go/no-go criteria. The pathways being investigated are alternatives to current fibers, boss materials, and liners, as well as methods to toughen resins.

- There is no indication that including hardware in the tank to enhance heat transfer to the storage media will be investigated.
- The project has balance of design and material improvement approaches.
- The approach given is weak because no solid metrics were provided by which to gauge the progress and value or contributions of this effort. By now, there is only a few months before the first go/no-go decision point in October of this year; no clear direction is evident that holds even the promise of getting us closer to the DOE system-level hydrogen storage targets. [DOE note: the first go/no-go decision point is scheduled for mid-FY 11 not October of 2010.]

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.4** based on accomplishments.

- The project lacks a sensitivity analysis of the relative gains in improvement; e.g., cheaper fibers. What the fibers are (only provides relative strength), and why there identification is this a secret was not provided. There are only a few fiber suppliers and most of the specifications are available publically. Lower safety factors should be addessed as well.
- The project started at a slow pace because of funding issues.Due to this problem, the progress is not very good. Materials issues and their characterization need to be addressed more critically. For example, why do other tests on fiber D if it has poor strength? If 7075 T73 is not good for bosses, look for other alternatives like titanium alloys for better specific strength and corrosion resistance.
- Tanks with alternative fibers have been fabricated for testing. The use of aluminum boss material is being investigated as are alternative liner materials. Different resin hardeners have been selected for testing. A stress rupture project is being considered with other collaborators. The purpose of the project will be to examine the increased data base for stress rupture of carbon fiber tanks with the intent to argue for a reduced safety factor.
- Baseline data needs to be presented in a format that allows for comparison against DOE targets. A better description is needed regarding how each work area; i.e., fiber, boss material, resin changes, and liner work, will potentially contribute toward improving metrics related to DOE targets. For example, what impact on product cost (in $/kWh) will a three-times more expensive liner material have?
- The PI describes a fair amount of structural development and tank testing but gives no clear indication of why they are doing what they are doing or to what end. The PI was not present during his poster presentation, and my discussions with the engineer manning the poster did not produce any insights as to what their contributions to the Engineering CoE were. He basically referred me to the PI, who was nowhere to be found!

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.0** for technology transfer and collaboration.

- Collaboration exists with the Engineering CoE, but it is not clear who the direct collaborating partners are (slide does not show) within the CoE.
- Collaboration with other efforts for material selection needs improvement.
- It does not appear that there has been a lot of interaction with the other members of the Engineering CoE. Guidance from the Engineering CoE, particularly concerning in-tank hardware requirements, is needed and could influence the paths being examined by Lincoln Composites.
- Project partners are identified, but it is not clear how they are participating or contributing.
- The PI gives the following as an indication of his collaborative effort, "collaborating on technical papers with John Khalil (United Technologies Research Center)—Lead, Kevin Simmons (Pacific Northwest National Laboratory), and Daniel Dedrick (Sandia National Laboratories)." No information was given as to the nature of the collaborative work and what was accomplished as a result of it.

Question 5: Approach to and relevance of proposed future research

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

- Continue work, but the approach needs to be defined.

- Not clear how lessons learned will be transferred back to Engineering CoE, and, if they will, be implemented in a tank build.
- The project plans look good based on the progress, but selection of the right hydrogen storage material is essential to the success of the project.
- Future work is only briefly described. No schedule is provided to show how the information from this project will support the Engineering CoE in preparing for the Phase I decision point.
- Future work is clearly identified, though more clarity regarding schedule is needed.
- The proposed future work given is very vague and general, as if it was copied down from their original proposal. It contains no metrics that they intend to meet and where they fit in with the overall Engineering CoE objectives.

Strengths and weaknesses

Strengths

- The institution and the PI are well known for composite materials development.
- Lincoln Composites has much experience in composite tank design and fabrication. They are an industrial partner and manufacturer of high pressure composite cylinders with existing product lines.

Weaknesses

- Expertise related to the role of materials to fatigue and corrosion is lacking.
- There does not appear to be a sufficient guidance from the Engineering CoE leaders regarding Lincoln's contribution to Engineering CoE's effort.
- The project does not sufficiently identify how the efforts, individually or in aggregate, are addressing barriers to reaching DOE targets.
- The value of their contribution to the success of the Engineering CoE is predicated on if a viable hydrogen storage material can be found that benefits from composite tank designs (at system level) without cost burdens.

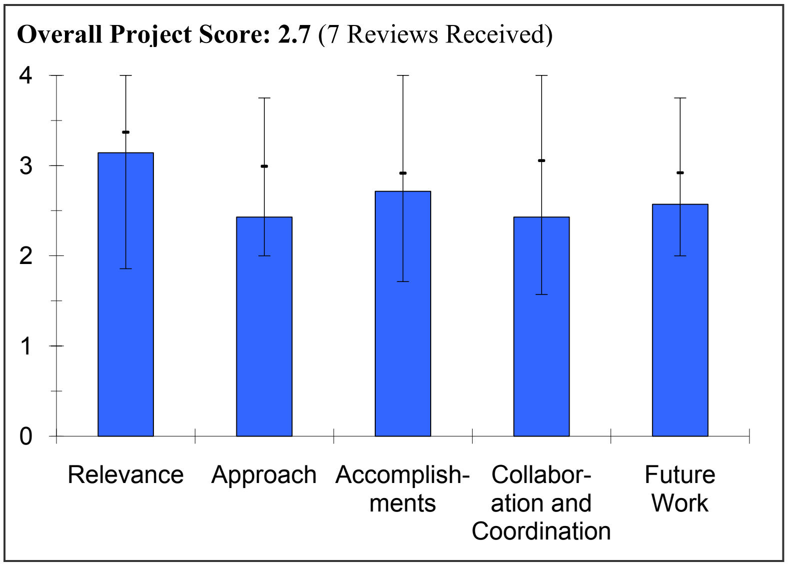
Specific recommendations and additions or deletions to the work scope

- Consider the implications of including heat transfer hardware in the tank.
- Revise the scope of work and give a solid rationale for why their contribution is needed or necessary.

Project # ST-48: Hydrogen Storage Materials for Fuel Cell Powered Vehicles

Andrew Goudy; Delaware State University

Brief Summary of Project



The objectives for this project are to: 1) identify complex hydrides that have the potential to meet DOE’s goals for storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions; 2) improve the sorption properties of systems that have been identified as good prospects for hydrogen storage; 3) determine the cyclic stability of new materials and develop strategies for improving reversibility; 4) perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time; 5) extend the studies to include other complex hydrides that have greater hydrogen storage potential; and 6) develop a viable storage system using flow, reaction kinetics, and thermal modeling, followed by system design, fabrication, and performance evaluation.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.

- The project is relevant to the Hydrogen Program's goals and objectives.
- The project involves a lot of metal hydride (MH) storage alternatives that have shown some promise yet have significant shortcomings. However, as models they may be useful.
- The project is in good alignment with DOE goals.
- The project is attempting to develop hydrogen storage materials of high capacity based upon magnesium borohydride and lithium borohydride destabilized systems.
- The materials chosen for this project currently operate at high temperatures (200°C-450°C), which does not enable them to operate with a fuel cell. However, it is necessary to study new materials systems and to understand the cause of the obstacles to be able to overcome the barriers.
- The project is well aimed at DOE targets and needs: weight and volume, desorption temperature, kinetic rates, etc.
- The project is focused on complex hydride reactions and, specifically, on capacity and kinetics, which are two of the major obstacles in this area.

Question 2: Approach to performing the research and development

This project was rated **2.4** on its approach.

- The approach is adequate for the goals of the project.
- The project would benefit by revising some of the model compounds that have been selected.
- Work should focus on mixed borohydirdes—other hydride systems are well focused. The need for studying a magnesium hydride system is unclear; it has been studied comprehensively in the past by numerous researchers.
- Is mechanical alloying the best way to make these materials?
- The researcher chose to use sodium alanate and magnesium hydride as "baseline materials" for comparison with the materials they are developing as guided by theory, which is reasonable. Magnesium hydride has been extensively studied in the literature and numerous additives/catalysts have been investigated, thus, focus should

not be on developing this material further, but on new materials discovery and development of new materials systems. Moreover, the borohydride related systems are "complex hydrides" and magnesium hydride is not, thus magnesium hydride and the complex hydrides are likely to behave differently.

- The approach has evolved over recent years and has taken better and more practical directions. That is, the PI has made good use of past data to move in new, more promising, directions.
- The acquisition of pressure-composition isotherms (PCT) is especially appreciated; most DOE projects do not make enough effort to get this important information.
- As much emphasis should not be put on magnesium hydride, even as a model system. There is so much historical data on magnesium hydride. Most of it suggests the system is not very amenable to very much thermodynamic modification. Kinetics is a different story, but also highly overworked.
- The choice of model system is not at all clear, both in terms of the system chosen, and in terms of the rationale for making this choice. Initially, it is stated that magnesium hydride is the model system, which does not seem like a particularly good choice and no rationale is given for why this was chosen. The history of this topic is very confusing; it is stated that in 2006, the model system was sodium aluminum hydride, and then in 2008 it was changed to lithium borohydride/calcium hydride, but in the initial slide of this presentation, the model system is stated as magnesium hydride. Further, it was then suggested that the choice of magnesium hydride is somehow related to the observation of reversibility in magnesium borohydride, but the connection between these two compounds is not at all clear.
- The PI chose six reactions based on magnesium borohydride to study for reversibility but it is not clear how these reactions were chosen, or how did the PI know what the expected products should be for these reactions. It does not seem as though there is a logical progression here.
- Some of the stated objectives of the progress appear to have almost no progress. It does not appear as though these items are being seriously addressed in the current project. There are essentially no results on these important points: 1) "develop a viable storage system using flow, reaction kinetics and thermal modeling, followed by system design, fabrication and performance evaluation"; 2) "perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time"; and 3) "determine the cyclic stability of new materials and develop strategies for improving reversibility."

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- Although the project's objectives are not met, it produced interesting fundamental results on the solid-state chemistry of metal borohydrides.
- This reviewer recommends the PI to take a closer look at solid-state transformations that generate polyboranes.
- Technical accomplishments have been good, even though only partial reversibility in all of the studied systems has been shown.
- Activation energies for lithium borohydride/calcium hydride stabilized with titanium (III) chloride seem quite high.
- Hydrogen capacities after cycling are significantly diminished from the magnesium borohydride systems.
- The lithium borohydride/calcium hydride system was investigated with respect to the additives’ effect on desorption temperature and activation energy, and they report a beneficial effect from using titanium (III) chloride. However, there is no attempt to explain the results, which is important to further advance the materials development.
- Six magnesium borohydride based systems were also investigated this year, based on theoretical guidance. Although three of them show reversibility, they are all high temperature systems with slow kinetics. It is recommended to perform a thorough experimental analysis of these three systems to be able to explain the reaction mechanism. It is also necessary to team with other research groups and use multiple tools, including X-ray diffraction, spectroscopy, neutron, synchrotron, and *in situ* studies.
- The third theme presented is on magnesium hydride and magnesium nickel hydride based systems with additives to enhance performance. It seems like the researcher is disconnected from other on-going efforts on the hydrogen program and there has been a few papers published from the Metal Hydride Center of Excellence (MHCoE) on magnesium hydride + titanium hydride mixtures in the past few years, thus, it seems less relevant to duplicate the efforts in this project. However, the results obtained are different as the MHCoE group found

that nanosized powders improved performance. It is recommended that Goudy, et al., also consider nanosized hydride mixtures as a complement to the additive study.
- Much useful and interesting data have been generated.
- The results on destabilized magnesium borohydride is interesting and potentially useful, especially the discoveries of partial reversibility at mild conditions. Again, the PC isotherms are especially valuable in understanding destabilization.
- The technical progress seems quite minor, given the length of time this project has been ongoing, as well as the committed resources. It is not even clear who is actually working on the project, and who is merely a (no-cost) collaborator. For $500,000 per year, there should be many PIs, students, and postdoctorates working on this project, and it is not apparent who is doing what with all this money.
- The PI stated that magnesium borohydride is reversible at less than 200˚C, but then showed no proof (or a reference) to this fact. It sounds very surprising and contrary to what others have seen in the field, and some evidence seems really necessary. Under technical accomplishments, the PI states, "we have determined that several destabilized borohydride systems based on magnesium borohydride can absorb hydrogen reversibly starting at temperatures less than 200˚C." This is a very important and provocative statement, but the PI didn't provide any evidence to this effect (specifically, that any material can 'absorb' hydrogen at temperatures below 200˚C. All the data shown is for desorption.It is expected that the work on magnesium hydride is probably not new. This material has been extensively studied, alloyed, etc., over the last 30 years. The PI should definitely do a better job of justifying the choice of magnesium hydride and placing this work in the context of the (considerable) literature in this field. For instance, the PI seems to think that these additions are "catalytic" and will reduce the desorption temperature. But, this presumes that magnesium hydride alone is not desorbing at the thermodynamic transition temperature, which it likely is. It is well known that the enthalpy of reaction (ΔH) for magnesium hydride is consistent with a thermodynamic desorption of about 300˚C, which is observed. It is not clear why one would add catalysts to decrease this temperature. One should add catalysts to increase the 'rate' of desorption. A lowering of the temperature would be an indication of a change in thermodynamics; i.e., a change in reaction, but not a catalytic effect.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.4** for technology transfer and collaboration.

- Surprisingly, no DOE research centers or national laboratories listed among the collaborators.
- Sufficient collaborations.
- Collaborative activities might be strengthened somewhat.
- It appears that there is a lack of coordination with other on-going efforts, and this needs to be improved in order to avoid duplication. Goudy, et al., would benefit from teaming with other institutions that have the research instruments needed to perform a more in-depth study of the materials under development.
- There are a few good collaborations; as indicated, the PI is looking for more.
- The very practical work being done in this project would be useful to the Hydrogen Storage Engineering Center of Excellence (Engineering CoE) objectives and activities. It is strongly suggest some formal collaboration be developed with this large group.
- Why is this project not a part of the MHCoE? It was started in 2006, so it seems as though it could have easily been incorporated (even informally) into the MHCoE. Some collaborations with other groups working on these topics could be quite useful.

Question 5: Approach to and relevance of proposed future research

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

- Future work proposal is reasonably good. The PI may think about dedicating some additional resources to studying the solid-state transformations of borohydrides.
- Future work is vaguely described.
- Modeling of kinetics has been envisioned for a long time, but as far as I can see, has not been done, and is proposed again.

- There is no need to concentrate on magnesium hydride (as proposed, "use various catalysts and combinations of catalysts to lower reaction temperatures and increase reaction rates. magnesium hydride will be used as a model system in these efforts.")
- At 7 years (began 2006, ends 2013), this is a very long-term project and it is not clear why it is so long?
- The effort on preparing and characterizing magnesium borohydride based systems should continue, preferably with theoretical guidance. However, based on the results presented here, it is recommended to turn to the results in the literature when using magnesium hydride as a model system, rather than spending time on experiments.
- It is recommended to add a task to focus on understanding reaction mechanisms of a selected promising materials system in order to learn about intermediate species forming and solid state phase transitions, as well as impurities forming, such as diborane coming off. With this knowledge, the reasons behind slow kinetics and high operation temperatures can be understood, which will guide further materials development.
- Proceed as planned.
- Overall, the project doesn't have good focus and justification for why the materials chosen are being studied. For that reason, the future work also doesn't seem to be well justified. Based on the progress to date, it does not appear likely that significant progress will be made in the future.
- The PI listed this as a 7-year project. (If this is a program that has been renewed, it would be useful to know this, and not to quote it as 50% complete over a 7-year span. [DOE note: this is a Congressionally Directed Project that was renewed in FY 09]

Strengths and weaknesses

Strengths

- The project has a strong materials science focus.
- High hydrogen capacity borohydrides are being considered.
- The magnesium borohydride and lithium borohydride stabilitized systems have the potential for high hydrogen capacities.
- The project strength is the focus on developing and improving high capacity materials that are challenged by slow kinetics and high operation temperatures.
- The PI has experience with practical hydride properties and evaluations such as PC isotherms, thermodynamics, kinetics, reversibility, etc.

Weaknesses

- The materials chemistry component has quite a bit of room for improvement.
- There is too much concentration on magnesium hydride, especially in repeating what has been already done.
- Significant reversibility issues and high absorption/desorption temperatures are still problem areas.
- There needs to be more focus on understanding the results by embarking on reaction mechanism studies. The project seems disconnected with other ongoing efforts and needs to coordinate better to avoid duplication. The project team needs to publish more peer-reviewed papers.
- The base hydride materials studied are not always very novel.
- It does not seem as though DOE is getting a very good return on its investment with this project. The investment is large, but the results are very minor, with no real insight to help improve these materials. In times of rapidly decreasing budgets, DOE cannot afford to dedicate a large amount of resources to a project like this.
- In the four years that this project has been ongoing, the PI has published two papers in the area. Both have zero citations (according to the Web of Science).

Specific recommendations and additions or deletions to the work scope

- The project team should consider elimination of the magnesium hydride work from the work scope; more focus should be on destabilized borohydrides.
- The project might benefit from chemical approaches to synthesize the destabilized materials.
- It is recommended to add a task for a reaction mechanism study that utilizes multiple sets of analysis tools and teaming with other groups.
- The work scope should establish at least a limited collaboration with the Engineering CoE.

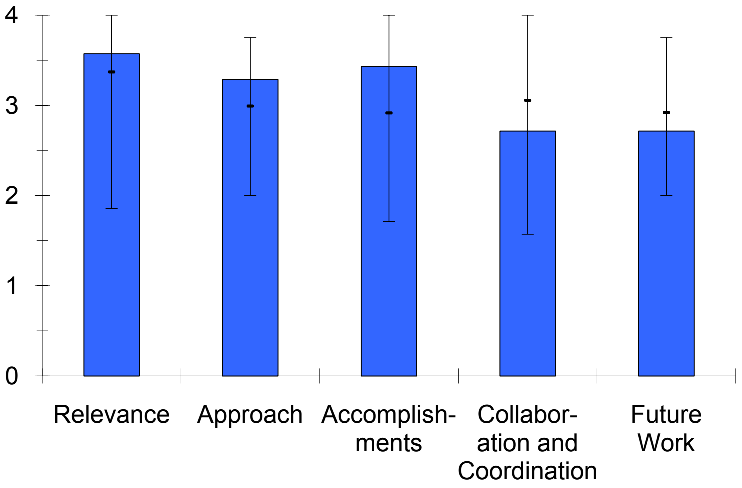
Project # ST-49: Hydrogen Storage in Metal-Organic Frameworks

Omar Yaghi; University of California, Los Angeles

Brief Summary of Project

The overall objective of this project is to increase hydrogen storage at room temperature. Objectives for fiscal year 2009-2010 are to: 1) implement "soft chemisorption" in the design and preparation of new metal organic frameworks (MOFs) with metal binding sites and with impregnation of metals and low-pressure measurements at various temperatures; and 2) prepare high surface area MOFs with preparation of expanded organic links, high throughput MOF synthesis, and activation of high surface area MOFs.

Overall Project Score: 3.3 (7 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- The project is relevant to the Hydrogen Program's goals and objectives. However, its focus started drifting away from the original goal, the high capacity hydrogen storage in MOFs.
- The project is adressing the development of new materials for hydrogen storage, some materials exhibit promising properties for transportation applications.
- The project seeks to develop MOFs with tailored metal sites for improved hydrogen storage capacity and binding energy. This goal is within the DOE objectives for hydrogen sorbent materials.
- The development of new, high surface area materials for hydrogen storage is essential to eventual practical applications; e.g., fuel cells. This work shows 1) incremental improvement in hydrogen uptake for new materials; 2) good reproducibility and reliability of the synthesis and measurements; 3) pursuit of some new ideas; e.g., metals incorporated into MOFs; and (4) progress in the scale up of MOF production. It is good to see that this work has not fallen victim to the seemingly irreproducible and spurious results of large hydrogen uptake in carbon based materials commonly known as the "spillover effect."
- High surface area materials are likely candidates for hydrogen storage if heats of adsorption and bulk densities can be improved.

Question 2: Approach to performing the research and development

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

- Approach has not changed from the previous year.
- Sharp focus on achieving storage density objectives. It would have been interesting to classify the materials in terms of cost in addition to effectiveness, and to discuss the possibilities of scaling production.
- A systematic approach to attach linkers which easily substitute to add platinum or paladium dichlorides is undertaken. A suite of characterization tools, including EXAFS, analyzes the platinum and paladium metal sites on the MOF-253 material.
- The approach of adding metal sites to the linkers in MOFs seems like a good approach, although it has proven to be challenging to de-solvate the final material to expose the metal site to hydrogen. It is not clear what the "high throughput MOF synthesis" approach is from the presentation.
- High surface area materials are obviously desired.
- The synthesis effort is good, but the project needs to add densification efforts.

- It is not clear that synthesizing compounds with ever higher surface areas will solve the hydrogen storage problem. This reviewer would prefer to see more of an emphasis on increasing diatomic hydrogen adsorption enthalpies. With this in mind, it is suggested that only the first of this project's two objectives is worthwhile.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.4** based on accomplishments.

- In general, the project produced quite a bit of very interesting basic results, which explains the "good" rating. However, it slowed down during the last two years. this reviewer did not find much new and exciting results or ideas in the poster presented at the AMR this year.
- The researchers realize that it will be necessary to shift from dichlorides of platinum and paladium to other ligand groups. The chloride groups inhibit hydrogen uptake.
- Regarding "high throughput MOF synthesis," it is assumed this is different from the scale-up effort, although it is not clear from the presentation. In any case, it is attractive to use some kind of high throughput or combinatorial approach to search for new materials, but an essential part of the technique is to have a rapid assessment of the result to see in a simple and easy way if there is something interesting. All too often, a "high throughput" approach means a rapid synthesis of lots of samples, or material, and it remains a laborious and tedious task to do the usual measurements and characterization of each sample. The real elegance of a combinatorial approach is really the measurement side of the process, to have a fast way to assess the products of the synthesis step for any interesting result that can then be followed up on.
- Good excess diatomic hydrogen capacity, but moderately high pressure and low temperatures are required.
- Efforts to develop MOFs with high capacity and high heat of adsorption have not yielded any materials yet.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.7** for technology transfer and collaboration.

- Collaboration is limited to just a few organizations and, surprisingly, does not include DOE CoEs.
- There were few specifics on collaborations. This reviewer questions why this project was not integrated with the activities of the Center of Excellence?
- There are few existing collaborations highlighted within this work. The poster lists collaborators in introductory slides, but collaborative results are not shown.
- Some collaborators are listed, but the presentation does not specifically indicate the contributions from them (especially Jeff Long and Bill Goddard). It is unclear what the various collaborators have contributed to the work presented.
- Collaborators are listed, but little or no description of their level of involvement is given.

Question 5: Approach to and relevance of proposed future research

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

- Not much is planned for the future. It is unclear if the PI is planning any research in the area after the project expires.
- The project is 90% complete—no comments here.
- There are plans to collaborate with a theory group for further developing the understanding of metal attachment and hydrogen uptake.
- The project ended April 30, 2009. There needs to be more elaboration on future work; only two bullet points on the summary slide were given, and they are not very complete.
- There should be a resonable extension of existing work.
- Not applicable because the project is complete.
- The two strategies for future research mentioned in the poster (slide 21 and reproduced below) are too vague to determine if anything novel is in fact in the pipeline.
  - Employ lightweight metals to create strong binding sites.
  - Material design based on theoretical prediction.

Strengths and weaknesses

Strengths

- This is a very strong basic chemistry project.
- A new promising class of materials has been identified.
- A systematic approach to improving dihydrogen binding energy by attaching linkers which may attach metal sites is good.
- There has been good work on improving MOFs for hydrogen storage produced, with innovative ideas about metal incorporation into the linkers.
- MOF synthesis expertise in this project is outstanding.
- Very interesting materials are used that are great for low temperature, (77 K) storage.

Weaknesses

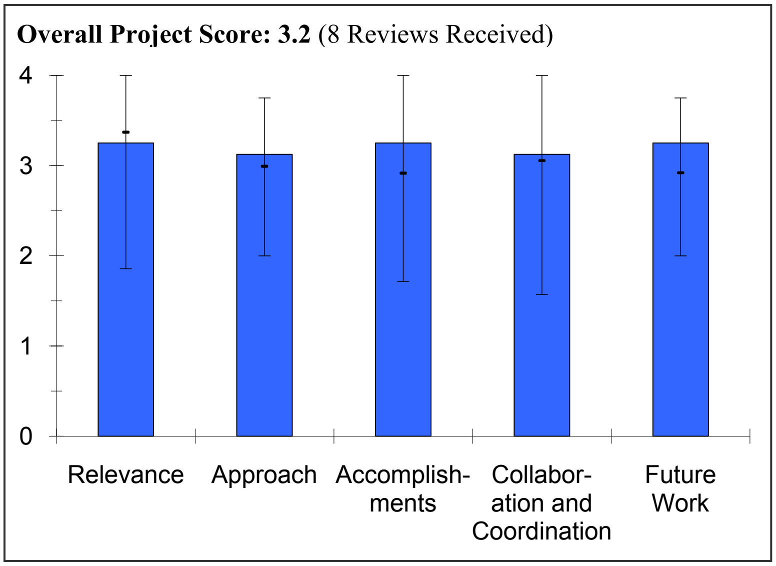
- The project has had limited collaboration and limited progress during the last two years.
- Lack of collaboration with other program participants.
- There were few collaborative results presented for this MOF project.
- It needs more explicit incorporation of collaborators' work in the project. More collaborators would strengthen the project. It is not clear what the "high throughput MOF synthesis" part of the project is, and what the results have been.
- Lack of efforts to make materials more practical (densification).
- Suitability for room temperature storage meeting DOE targets is highly questionable.
- There is an impression that this project is taking too much of a "try this and see what happens" approach and lacks a clear strategy.

Specific recommendations and additions or deletions to the work scope

- Identification of other applications beyond storage—hydrogen purification, carbon dioxide sequestration, storage of natural gas, etc.
- Develop collaborations with a theory group (as planned).
- More attention to relationship between surface area and hydrogen storage would improve the scope of the project. Something more involving combinatorial studies of MOFs, particularly with regard to how to rapidly assess the materials produced, would be a great addition to the project in the future.
- Screen methods to pelletize or use other methods to provide physically usable sorbents.
- Not applicable because the project is complete.

Project # ST-50: Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

Di-Jia Liu; Argonne National Laboratory;



Brief Summary of Project

The objectives for this project are to: 1) design, synthesize, and evaluate nanostructured porous organic polymers (POPs) as new hydrogen storage adsorbents for transportation applications, and 2) support polymer materials development with modeling/simulation and advanced structural characterizations.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- This projects aims the development of nanostructured POPs as new hydrogen storage adsorbents.
- The development of high surface area polymeric materials opens up a wide option of new materials for physisorption storage and is very relevant to DOE goals.
- POPs are good complement to other high surface area sorbent areas,including metal organic frameworks (MOFs),in the program.
- The project's objectives are relevant to the hydrogen storage goals. The project explores the potential of a new class of materials called POPs for hydrogen storage applications.
- Project objectives highly relevant to the DOE RD&D objectives in regards to the synthesis and evaluation of sorbent POPs for on-board storage.
- Project focuses on demonstrating improvements to volumetric density, a key barrier associated with this class of materials.

Question 2: Approach to performing the research and development

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

- The pressure to make a material that does it all has lead to a wealth of new POPs, and the PI has focused down on some of these materials that show potentially beneficial characteristics. The sheer number of materials listed makes it difficult to see if they have any type of adsorption characterization on all of them, and hence look for trends amongst the different monomer/treatments they have performed. Of those selected to be presented, the application of the right characterization tool to the issue at hand seems to be well thought out and input of theory when needed on top of this. The work is focused on both addressing pore sizes and increasing enthalpy of reaction (ΔH) through metal incorporation.
- The approach is consistent and builds on previous progress.
- The synthesis work is clearly very strong. More focus and collaborative support on hydrogen sorption characterization is needed.
- Experimental efforts are being guided by theory and insight.
- The approach has good synthesis and materials modifications strategies.
- Competency in characterization and sorption methods are an asset.
- The project's approach is well balanced between theory, experimental synthesis, and characterization of these materials. However, it is not clear how the project ultimately plans to reach the capacity, especially if metal doping is necessary to raise operating temperatures. Same challenge applies to almost all the carbon based adsorbents.

- Approach to materials discovery and development is ideal, involving novel, “rational” materials design and synthesis, property characterization and optimization; i.e., structured experiments to identify trends, and modeling/simulation for streamlined experimental efforts. The approach is structured and flexible and the goals are specific; e.g., forming POPs with high surface area and narrow/adjustable pore size. It is great to see that the project aims to understand structure-property relationships at a fundamental level.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.3** based on accomplishments.

- A dazzling array of materials has been synthesized and partly characterized (at least in terms of surface area) with some of the higher surface areas for these types of systems and spectacular control of the pore size and distributions. The uncertainty in what is required to make the best storage system makes this work a good candidate for cryogenic, or even intermediate-range temperature storage materials, but is unlikely to contribute to a room temperature tank beyond adsorbents already known. There could be some advantages in the polymer processing of these types of materials over activated carbons, however, and that aspect should be borne in mind.
- Efforts to increase ΔH have taken several routes, most with modest increases evident, but while still maintaining a remarkably high surface area and cryogenic storage capacity in several systems.
- This project led to the development of POPs that are clearly still inferior to the state-of-the-art activated carbons and MOFs. The volumetric storage capacity of these material is still an unknown quantity, and the PI is encouraged to give some results in this area, or at least the bulk density of the synthesized materials. Their compressibility without structural or capacity loss is assumed but yet to be proven. It is highly unlikely. Moreover, the PI repeatedly presents his materials as having higher binding energy. He is only presenting data at low pressure (low coverage) where the binding energy is initially high for all adsorbents. He really needs to extend his calculations to higher pressure (meaningful coverage) and compare with activated carbon and MOFs.
- Significant accomplishments have been made in synthesizing a number of new nanostructured polymeric materials with variations in pore size, metal and non-metal doping, and modified adsorption enthalpies.
- The ability to demonstrate the ability to tune the micropore is very good progress.
- The ability to dope the polyporphyrin based POP (PTTPP) with iron and show an enhancement in the heats of adsorption is also very good.
- Synthesis of boron-containing and metalloporphyrin polymers is significant achievement.
- The strategy for fine tuning POP structure and nanopore architecture has yielded significant increases in heat of adsorption. The results agree with theory.
- Capacities are still low compared to targets.
- Given that the project is in the middle of its cycle and that this is a new research area, the project has made excellent progress.
- The ability to synthesize and control the material pore size and reliable characterization is significant.
- The improved heat of adsorption with transition metal doping without sacrificing pore size is an interesting result.
- A variety of diverse POPs were prepared. It was clear this project was deliberately structuring experiments to improve key challenges with sorbents, for example utilizing porphyrin-based monomers with various transition metal cores.
- Correspondingly the impacts of metal cores on the hydrogen uptake and ΔH were analyzed. The fluid connection to theory was also demonstrated by modeling POPs with various transition metals. Finally, it was great to see an evaluation of pore size and the optimization/tuning of pore structure based on using various aromatic monomers. Overall, the project has made great progress with well thought out experiments!

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- There is certainly strong collaborations within this team of people, and their presence in the Hydrogen Sorption Center of Excellence (HSCoE) is likely a boon for them over the past few years, and focuses the results toward addressing DOE goals. While it is clear that there are different functional arms of the collaborations, the cross-fertilization between theory and experiment and synthesis seems to be present allowing for a well run team.

- There are strong collaborations with industry, the National Renewable Energy Laboratory (NREL), and universities on synthesis and measurements.
- There are good collaborations within and outside the Center.
- There is an appropriate level of collaboration.
- The project is leveraging expertise of the University of Chicago subcontractor, and is interacting as part of the HSCoE. Various other collaborations are evident, for example, for characterization and measurement validations.

Question 5: Approach to and relevance of proposed future research

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

- The addition of a go/no-go decision point will keep the program on track to address the DOE goals. The work seems now more sharply focused on addressing high ΔH materials, and, in the coming year, looks like it will capitalize on these improvements and look at the materials science problem of volumetrics.
- The project has a built in go/no go decision for next year.
- Future work is consistent with project goals.
- Special consideration should be given to the possibility of POPs pelletization.
- There is a reasonable extension of current work.
- Future plans look good.
- Project team gets high marks for highlighting measurable go/no-go decision point; although, they should also have specified the working pressure with the gravimetric and temperature targets.
- Well-planned future studies which are a continuation of current results. It is great to see a timeline of work intended for the remainder of this year, as well as going forward into next year.

Strengths and weaknesses

Strengths

- The diversity of sample synthesis, characterization, and computational skills in the team and through collaborators. Also, the enormous productivity of new materials combined with the in-depth focus when warranted.
- New type of storage materials are being used.
- Developing the ability to tune pore dimensions and maintain high surface area is a great accomplishment.
- The ability to tune the micropore is very good progress.
- The ability to dope the materials with iron is very good.
- Polymer synthesis and good adsorption work.
- The project area of research is new.
- The project team presented the positive progress made as well as the challenges in context by plotting hydrogen uptake curves at 77K and 298K in the same plot. This may sound trivial, but it is important that the PIs, students, and reviewers all keep in mind the intermediate achievements relative to the ultimate target.
- It is a very organized and focused project that is making great progress. Novel materials focused on addressing sorbent challenges, e.g. improved binding, are being studied.

Weaknesses

- Alas, some of the strengths are also weaknesses. The prolific nature of the materials synthesis likely does not allow for a full and deep understanding of what they have actually managed to achieve in producing these arrays of materials. This is somewhat of a problem with the applied nature of the program where the end goal is the only thing that matters, but it seems like a waste of a learning opportunity.
- The project has not given a clear explanation for the unusual shape of the physisorption isotherms.
- The project needs to address the ability to increase capacity.
- Pelletization and finding ways to enhance the volumetric capacity is needed.
- The research topic is of a difficult nature.

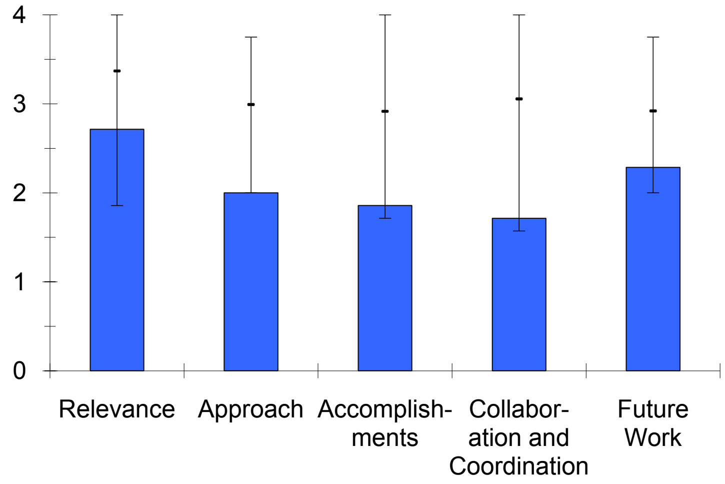
Specific recommendations and additions or deletions to the work scope

- Allow some scope to investigate more the differences and similarities between new materials and the effects on diatomic hydrogen uptake characteristics.
- Post-treatment methods (heating) seems to have made the most impact on changing adsorption enthalpies. Reviewer recommends focusing efforts on these post-treatment options in combination with the increasing surface area of the primary materials.
- Reviewer recommends collaborative testing of these materials such as dielectrics in capacitance-assisted diatomic hydrogen storage project ST-026.
- Keep the current project; however, it is recommended to start considering finding ways to effectively enhance the volumetric capacity.
- Increase polymer characterization/physics to better understand heat treatment of boron containing materials.
- The potential cost advantage of POPs (if any) should be highlighted when comparing their performance against similar materials such as MOFs.

Project # ST-51: Electron-Charged Hydrogen Storage Materials

Chinbay Fan; Gas Technology Institute

Overall Project Score: 2.1 (7 Reviews Received)



Brief Summary of Project

The overall objective for this project is the development of a hydrogen storage material and device for hydrogen quick charge and discharge, high percent weight (wt%) and percent volume (vol%) storage capacities, good durability over many cycles, and safe handling and transport. The 2009 objectives are to: 1) reselect the best hydrogen storage materials for charge modifications; and 2) develop carbon-based materials, such as AX-21 and other high surface carbon using polymer as precursor, metal-modified carbon, and ammonia borane (AB).

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.7** for its relevance to DOE objectives.

- There was no articulation in the presentation stating, except in the broadest terms, the project’s goal, so it is impossible to judge on the scientific or technological merits what the Gas Technology Institute (GTI) is attempting to do.
- This project is based on the interesting idea that introducing a new thermodynamic variable to control the properties of a solid-state storage unit for hydrogen.
- The project is relevant to DOE objectives and utilizes external electron charge effect on increasing fueling rate and capacity of hydrogen charging..
- This project uses an applied electric field to improve hydrogen uptake in carbon (physisorption), metal hydrides, and AB. This is a unique approach and appears to improve hydrogen gravimetric capacity.
- The project "Electron-Charged Hydrogen Storage Materials" seems far fetched to overall DOE objectives.
- The project is generally aligned with the aims of the program; however, it takes a very high risk approach.
- This project employs a unique and entirely unconventional approach for hydrogen storage. Although, in this reviewer’s view, the project is a “long shot” for meeting DOE targets; it is aligned with DOE objectives and it has sufficient novelty and potential to justify continued support.

Question 2: Approach to performing the research and development

This project was rated **2.0** on its approach.

- The approach slide shows a heating and cooling coil connected to a Sieverts. There is no explanation as to what has been done in this work and what the system that is connected to the Sieverts is meant to accomplish. As a schematic, there appears to be nothing unique in this configuration.
- The project suffers from a lack of guidance from either theory or simulations, particularly in the way the materials are selected. Specifics on the mechanisms should have been given in the presentation, and a discussion on how materials selection was performed based on those mechanisms.
- The approach of the project is to test different materials in Sievert-type thermal gravimetric analysis (TGA) stations for the effect of external electron charge on hydrogen adsorption/desorption kinetics.
- The electric field is applied within a Seivert's apparatus concurrently with increasing pressure. The research has isolated the effects of heating and cooling from increased applied voltage.
- The approach seems very sketchy relating to selection and synthesis of carbon-based materials.
- Use of electrochemistry to attack the problem is worth trying.

- Materials are good from a mass basis (carbon) to questionable (metal hydride).
- It is not clear if they have deep understanding of how this works. They certainly could not explain it well in depth.
- An approach has been adopted that uses both internal electron charge (doping) and external charge to alter the electron distribution in a hydrogen storage medium, thereby enhancing electrostatic attraction of hydrogen to the substrate. It is suggested that enhanced hydrogen adsorption occurs via induced dipole interactions between the charged substrate and the hydrogen molecule. However, the approach is highly speculative, and very little theoretical work has been performed to support the notion that improved hydrogen storage yields can be expected under practical current and voltage conditions.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **1.9** based on accomplishments.

- Slides 8 to 12 show pressure-composition isotherm (PCT) curves, but do not specify the metal used, what the numbers in the plot mean, or what the data show.
- It is unclear what does the weight loss in slide 13 means.
- Unfortunately, none of the slides have any meaning as there is no explanation of what is being measured and what the measurements might mean and what the motivation for the measurement approach might be.
- Although interesting effects are observed, they are somewhat marginal at ambient temperature, occurring at relatively low pressures (in the sense of the DOE storage targets for hydrogen) and disappearing at pressures of interest for storage applications.
- Very minor progress was made, few PCT curves of unknown material show minor increases in capacity;no data on the effect on kinetics were given.
- Many results were shown that show the applied electric field is successful at improving hydrogen capacity. The PI is in the process of validating these experimental results with several more trials.
- The results obtained so far do not look promising.
- The project has generated some data, though a bit low for one year.
- The graphs were mismarked, which may confuse reviewers.
- The increase in capacity is a good accomplishment, and note that the usable amount increases, too. This needs to be confirmed.
- Also claim to regenerate AB in this process.
- The basis of the extended hydride capacity is thought to be filling metastable states with energy too high to fill with moderate pressure.
- Only minor improvements (~20%) in storage capacity have been observed in a metal hydride (microporous AB on different support substrates) during electron charging. Additional work has recently focused on boron nitrides. However, results thus far are not particularly promising. No analysis has been performed to predict what actual storage capacities might be expected under the operating conditions used in these experiments. Overall, there has been only limited progress on this project since the last review.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **1.7** for technology transfer and collaboration.

- It is not clear what the nature of the interaction with other groups is, save for taking a few measurements.
- Not enough detail on the collaborations were provided.
- This reviewer is not clear at all on what sort of collaborations the PI had.
- There is no clear indication that this work is done collaboratively.
- Not much collaboration with Hydrogen Storage Engineering Center of Excellence partners.
- Several groups are named, but it appears that there is limited collaboration with them. Still they are on a fairly different sort of project, so that is not a terrible thing. Ought to compare data with the Los Alamos National Laboratory.
- Only limited collaborations are evident. It’s not totally clear what contributions are being made by the cooperating institutions.

Question 5: Approach to and relevance of proposed future research

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

- Given the lack of detail in what GTI has accomplished, the goals, as set forth in the proposed work, lack context.
- The project seems to emphasize enhanced kinetics in borohydrides, and seems to conclude that little benefits are to be expected for enhanced storage capacity.
- The proposed future work is nothing more than continuation of the previous work, probably with the same limited success.
- The PI is looking to scale up to a 11-liter tank and move to the higher capacity system, AB. These are both worthy future plans.
- Changing from carbon-based materials to boron nitrides for external charge bias to increase the hydrogen storage rate is not clear.
- The key is the large scale tank and confirmation outside.
- Proposed work calls for scale up to an 11-liter tank. However, given the paucity of experimental data and the lack of theoretical results obtained thus far, it seems premature to propose a scale-up task. The continuation of the boron nitride work is probably worthwhile, but a more definitive statement about how the experimental work will actually be done is important. A forthright presentation of barriers and obstacles that must be overcome in order to achieve high capacity storage by this method is needed. Finally, plans in place to address those challenges should be presented.

Strengths and weaknesses

Strengths

- None.
- This project is based on an interesting idea, that of introducing a new thermodynamic variable to control the properties of a solid-state storage unit for hydrogen.
- The project tries a new engineering approach.
- The project ideas are unique and may effectively lead to alternative means for improving hydrogen loading.
- The PI has good background in electron shift (physisorption) and electron transfer (chemisorption).
- The project approach uses a very “out of the box” idea.
- The project will open a large new area of research if successful.
- A novel approach to enhancing hydrogen adsorption in a reasonably simple experimental system is proposed.

Weaknesses

- The nature of the work is of no value to the program as slides of data with no explanation are presented. The presentation needs to be self explanatory and not have to rely on questioning at the poster session as to the details of the work being presented.
- Although interesting effects are observed, they are somewhat marginal at ambient temperature, occurring at relatively low pressures (in the sense of the DOE storage targets for hydrogen) and disappearing at pressures of interest for storage applications. The results should also be validated by another group, and I did not see results at 77 K, which would help show whether the enhancement observed depends on a low level of filling of the pores (as suggested by the high pressure room temperature results). This reviewer also feels that there is a lack of theoretical guidance as observed by another reviewer. Referring to nanotubes as theoretical justification is a bit restrictive, taking into account the specific properties of these carbon nanostructures, which are very different from the other structures investigated in this study.
- The project shows limited improvements, and is lacking of theoretical justification and predictability.
- There is not an adequate assessment of energy balance; i.e., the amount of energy required to apply the voltage during loading relative to the amount of improved hydrogen capacity).
- The theory is not clear for the experimental design.
- The project team needs to confirm that the theory is right so that they can move foreward rapidly.
- The project team needs to figure out how to apply the process to materials with a much higher capactiy, as a small increase in a 2% material is not going to make progress toward meeting the goals.

- The PI could not explain exactly how the hydrogen is pegged to the voltage.
- There is a lack of a predictive theory or model to guide experimental effort; experimental results obtained thus far are not promising.

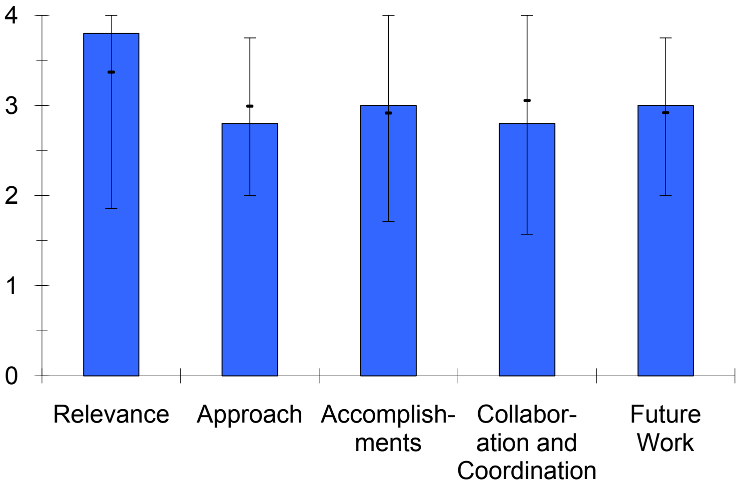
Specific recommendations and additions or deletions to the work scope

- This project appears to contribute nothing to the program, and I strongly urge that the project be suspended.
- This reviewer recommends calculations that show that the amount of energy gained from the additional hydrogen stored due to the applied voltage is greater than the amount of energy used in applying this voltage.
- The absolute first priority is to load a hydride and to have it tested outside to confirm the electrostatic influence does increase capacity over normal pressure loading rates.
- I would suggest doing a full capacity enhancement demonstration in which one polarity is applied in loading and then reversed in unloading to demonstrate the highest capacity accessible between 2 bar and 350 bar.
- It is critical to thoroughly and straightforwardly articulate the obstacles and challenges that have been identified in the experiments thus far, and to explore possible mitigation strategies. Reviewer recommends that the scale-up task be deleted or postponed until more definitive experimental results on a small-scale system are obtained.

Project # ST-53: Lifecycle Verification of Polymeric Storage Liners

Barton Smith; Oak Ridge National Laboratory

Overall Project Score: 3.1 (5 Reviews Received)



Brief Summary of Project

The project goal is to perform durability qualification measurements on polymeric tank liner specimens and assess ability of liner materials to maintain required hydrogen barrier performance. Milestones for 2010 are to: 1) complete thermal cycling and permeation measurements in Lincoln Composites liner materials; 2) complete thermal cycling and permeation measurements in Quantum Technologies liner materials; 3) complete measurements of hydrogen solubility, uptake, and the effects of hydrogen-induced swelling in tank liner materials; and 4) make a go/no-go decision on the acceptability of existing liner materials.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.8** for its relevance to DOE objectives.

- The project "Life Cycle Verification of Polymeric Storage Liners" is relevant to overall DOE objectives because the durability of polymeric tank liners over the performance lifetime of high pressure storage systems must be verified and validated.
- Liner performance is critical to performance of early stage tanks.
- Storage costs are an important element with respect to enabling cost effective on-board hydrogen storage and, therefore, hydrogen vehicles.
- The project has important relevance in assessing the performance and safety of type IV pressure vessels. There has been work in the area of evaluating metals through hydrogen embrittlement work. This project focuses on testing the performance of polymers over the cycle life, which is very useful.

Question 2: Approach to performing the research and development

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

- The approach to follow the Society of Automobile Engineers (SAE) International technical information report J2579 to develop and carry out durability test cycling measurements is good. A critical approach to address the shortcomings of SAE J2579 will be relevant.
- Good experimental apparatus and protocol for addressing problem.
- The approach is well conceived and based on industry developed standards and performance requirements.
- The general approach is fine but appears to have some areas that could be improved:
  - Consider if the bench test results could be validated against a complete cylinder; i.e., test a sample from a cylinder that completed cycling in a laboratory or in the field.
  - Consider providing further details on the test method to help the codes and standards organization develop a material permeation test.
  - Confirm theories with models or other analysis for cycling effect.
  - Include additional materials beyond standard liners to evaluate their potential.
  - Include expanded temperature range such as -40˚C and lower and potential for exceeding the traditional 85˚C maximum.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- It is good to see completed permeation measurements through 2,000 cycles that show no statistically significant departures from Arrhenius relationship and no microcracking or changes in glass transition temperature in the polymer. Analysis of activation energy indicating that the polymer is undergoing microscopic changes in polymer matrix will be helpful for future work.
- The effects of aging are clear.
- The work to date has indicated that current materials are meeting performance expectations. Information regarding performance relative to DOE targets should be provided.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.8** for technology transfer and collaboration.

- Collaboration and coordination with other institutions such as Lincoln Composites, Quantum Technologies and Ticona are helpful for the project.
- Very little collaboration is evident, but it may not be needed in this project.
- This type of effort does not require a significant amount of collaboration, but it would be helpful to understand how container manufacturer participants are contributing (aside from liner samples).
- It seems like there could be some collaboration with the Hydrogen Storage Engineering Center of Excellence.
- The collaboration partners appear to be the industry leaders in type IV tanks. Since this project is focused on testing of materials, it may be useful to consider including or consulting with hydrogen test facilities to compare lessons learned. It would also be useful to provide or present the project to SAE and other standards organizations for feedback in the testing method.

Question 5: Approach to and relevance of proposed future research

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

- Future works to verify initial lifecycle measurements including temperature cycling at 860 bar and 430 bar pressurization are going to be helpful.
- Continuation to max cycles is a reasonable extension.
- The work is well structured and scheduled.
- The future work is focused simple on testing. The work should also include an attempt to validate the results, understand the root cause effecting the polymers, transfer knowledge to codes and standards organizations, and assess potential of other materials.

Strengths and weaknesses

Strengths
- The Institution and the PI are well placed for the project.
- Good component-level assessment work.
- The project covers a needed area of research in assessing and comparing polymer materials in a hydrogen lifecycle evaluation.

Weaknesses
- Additional insight into tank liner materials for measurement of hydrogen solubility is necessary.
- It needs to be made clear that the project is addressing a problem the industry actually has.

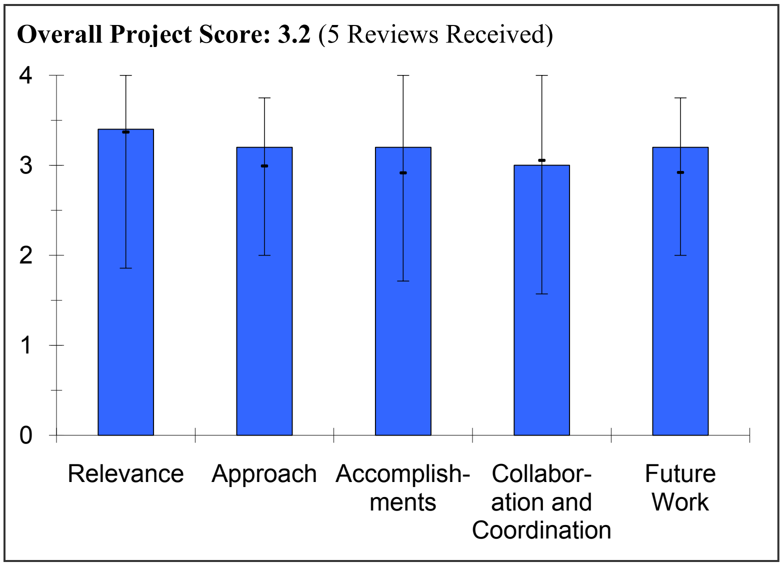
Specific recommendations and additions or deletions to the work scope

- Work with polymer physicists to ensure maximum information is gained from postmortem analysis. For high density polyethylene (HDPE), analysis should include nuclear magnetic resonance, thermomechanical analysis, etc. Polymer producers (Chevron, ConocoPhillips, ExxonMobil, and others) should be consulted since they are the most likely to have state-of-the-art HDPE characterization.

- Overall, it's not clear if anything useful is being learned at the materials level, as it is not clear that characterization of the Lincoln Composites and Quantum liner materials compositions is being done or is allowed.
- If these materials are proprietary, it is unclear how the degradation mechanisms will be made public.
- While it's important to know if durable tanks (and their liners) can be made, This reviewer has the impression that this is an analysis that Lincoln Composites and Quantum ought to be performing at their own expense.

Project # ST-54: Standardized Testing Program for Solid-State Hydrogen Storage Technologies

Michael Miller; Southwest Research Institute.



Brief Summary of Project

The objectives for this project are to: 1) support DOE’s Hydrogen Storage Program by operating an independent national laboratory aimed at assessing and validating the performance of novel and emerging solid-state hydrogen storage materials and full-scale systems; 2) conduct measurements using established protocols to derive performance metrics for capacity, kinetics, thermodynamics, and cycle life; and 3) support parallel efforts underway within the international community, in Europe and Japan, to assess and validate the performance of related solid-state materials for hydrogen storage.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Conducting accurate storage measurements is extremely difficult and subject to much error. The program needs a gold standard, independent facility to validate results from many different sources. The Southwest Research Institute (SwRI®) has established themselves as the gold standard.
- The project at SwRI® is primarily to serve as an independent measurement center for the DOE/EERE Hydrogen Storage Program, rather than to discover or develop new storage materials. They do serve an important function in the program to determine whether the claims made by other research groups are valid or not, which helps DOE to make go/no-go decisions and not spend its limited resources on unproductive candidates. SwRI® also reported at the AMR some of their own in-house and collaborative studies on potential hydrogen storage materials. This work is useful to the program, even though the recent materials do not appear to have the ability to meet targets.
- The need for standardization is great.
- This project is focused on establishing a standardized and robust testing procedure for hydrogen storage research. This is an extremely valuable element of the DOE program because reliable, reproducible results are essential for progress to be made in achieving DOE's goals and objectives.
- This effort indirectly supports DOE targets and plans, especially in the properties of weight, volume, thermodynamics, and cycle life.

Question 2: Approach to performing the research and development

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

- Generally good— This reviewer is always somewhat confused by what proportion of effort is expended between DOE required samples and their own samples that they test and if one impedes the pace of the others. The PI should make a statement on what the throughput limitations for the laboratory are.
- Over the years, SwRI® has set up their analytical capabilities to assess the hydrogen storage capacities by both gravimetric and volumetric methods as well as to establish capabilities to prepare some types of materials and perform complementary measurements. For future work, SwRI® should make available to the general hydrogen research community via webpage links to their complete analytical capabilities and measurement procedures.

This may help to better standardize characterizations by other research groups - note the wide discrepancies for sodium aluminum hydride isotherms shown on slide 11.
- The basic philosophy of this project is to provide a national source of testing, verification, and other contributions. This is clearly important.
- The work appears to be a mixture of DOE-directed efforts, international (DOE-supported) support, private jobs, and SwRI® work. This is an acceptable approach if DOE contractors cannot provide an adequate number of samples to maintain a full-time presence at the facility.
- This project would be better if it focused more on identifying what results are accurate, what measurement techniques are needed to ensure accuracy for these kinds of measurements, and how differences in reported data can arise.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Progress can't be judged by number of samples tested at this point, as it can only progress as fast as they come in. Some samples need significant equipment modification and preparation time. Perhaps the PI could give an idea of how many samples are in the queue and what the average throughput rate is and is there a chance for improvement?
- The PI has done a great job adjusting test equipment as necessary to accurately understand and measure new materials.
- SwRI® either completed or is conducting the verification measurements requested by the DOE during fiscal year FY 10. It would have been good to see the status of measurements that were scheduled to be finished by June 2010 as shown on slide 18.
- The only DOE-directed testing at SwRI® in 2010 has been to evaluate the effect of a piezo-induced charge on hydrogen adsorption in nanoporous carbon. The results indicated that there was no measurable increase in hydrogen adsorption from the charge accumulation, at least under the SwRI® test conditions. These results tend to refute the claims by Michigan Technical University. The cause for the different results was not presented.
- There are inconsistencies in the pressure concentration temperature (PCT) data in the novel efficient solid storage of hydrogen (NESSHY) round-robin testing that indicate more work is required to develop standard guidelines for experimental procedures to ensure that results from multiple institutions can be compared.
- The results shown do not bring us closer to meeting DOE system targets.
- The internal work does not appear to have much relevance to the DOE program objectives.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- The project team is working with the appropriate partners. The PI would be encouraged to maintain an open dialogue with original equipment manufacturers (OEMs) and other experienced experts in measurements.
- SwRI® has interacted mainly with members of the Hydrogen Sorption Center of Excellence (HSCoE) for DOE. They have had a least a couple of external collaborations on other possible storage materials. If SwRI® is to be the DOE source for standardization of hydrogen capacity measurement, the reviewer would like to see an indication of close cooperation with Dr. Karl Gross, who has compiled extensive documentation and reviews of the requirements and limitations of obtaining reliable results. This reviewer does not know whether this has occurred in the past or is planned for the future.
- Given that SwRI® is also having an internal materials program, i.e,. paladium/silica spill over, it is recommended that SwRI® work closely with other groups within the HSCoE to avoid any overlap.
- By nature, the HSCoE is extremely collaborative.
- This project has a very good collaborative research portfolio.
- The standardization and round-robin testing should have a positive impact in reducing error in the results obtained in different laboratories. The round-robin results indicate that independent measurements are not completely comparable; more work is needed to sort this out.

Question 5: Approach to and relevance of proposed future research

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

- The project team should continue to test samples as they come in.
- A significant portion of the SwRI® efforts are at the specific requests from the DOE to provide independent measurements on an as needed basis. Hence, this work load can be very variable and did not seem to be very large in FY 10, but there was no indication of what will be needed in FY 11.
- SwRI® also has an internal materials program, and, therefore, it is recommended that: 1) they continue to focus on materials diatomic hydrogen sorption measurements, and 2) they focus on spillover mechanistic understanding rather than materials synthesis; i.e., collaborate with the synthetic groups within the HSCoE for materials preparation.
- Excellent concentration on technical goals.
- The project will end in 2011. Final samples are expected from the materials CoEs. It is important that the results are conveyed to the HSCoE in a timely matter.
- It is not known how many samples will be sent to SwRI® for analysis by the CoEs as they wrap up and prepare final reports. This could result in SwRI® running short on funds before all of the samples of the "best" materials can be tested.

Strengths and weaknesses

Strengths

- SwRI® has, over the past several years, established a laboratory capable of evaluating a wide variety of hydrogen storage materials. They appear to provide timely response to DOE for requested services.
- Performance of some independent research on hydrogen storage systems is useful to broaden the experience of staff and to extend the range of capabilities.
- Analytical measurement capabilities are good.
- The project is addressing a critical need for standardization.
- Standardized testing procedures are essential to good research on hydrogen storage materials, and this project is all about that.
- The concept of having a national testing laboratory is, in principle, sound and valuable to DOE and the entire storage materials community.

Weaknesses

- Other than some contact with the HSCoE groups, SwRI® has not seemed to be come involved with most other DOE hydrogen storage projects. More open communication would have been beneficial.
- It was not clear whether measurements performed at SwRI® were being subjected to oversight from other highly experienced individuals on hydrogen storage materials and the state-of-the-art measurement techniques used elsewhere.
- Collaboration with others with regards to the spill over materials research.
- None.
- It is not clear if the results so far have improved the general, national, and worldwide accuracy of testing.
- There seem to be a number of independent activities being pursued without clear justifications other than that the DOE storage projects are not providing a sufficient number of samples to fully utilize the facility.

Specific recommendations and additions or deletions to the work scope

- It is recommended that a more or less formal review be held of SwRI®'s current capabilities and recent results. It is not that there are any expected deficiencies with the SwRI® work, but a peer review would serve to confirm their capabilities and potential value to DOE and outside groups involved with hydrogen storage materials. It is also suggested that SwRI® contact the DOE/EERE Engineering CoE to see if SwRI® could provide some of the additional physical and chemical properties needed for comprehensive modeling over the next few years.
- Keep the project as data validation is very important.
- The project will be ending soon. The physical state of the facility needs to be assessed to determine if it is worth maintaining beyond the end of the program.

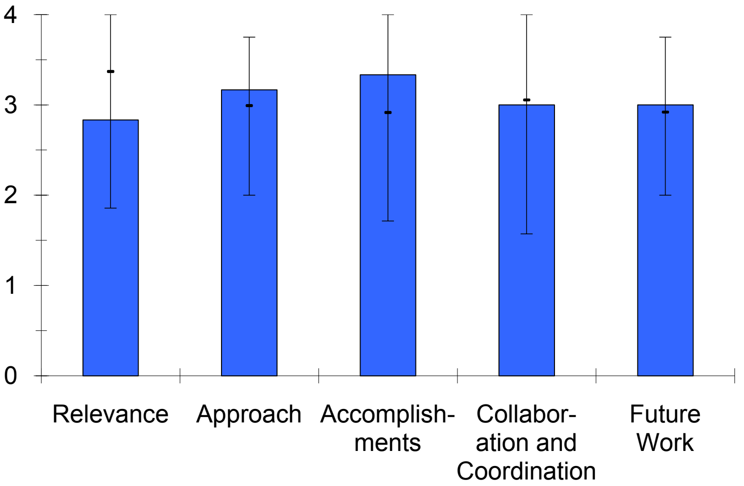
Project # ST-55: NaSi and Na-SG Powder Hydrogen Fuel Cells

Michael Lefenfeld; SiGNa

Brief Summary of Project

The objectives for this project are to: 1) demonstrate enabling hydrogen storage technology suitable for early fuel cell (FC) market applications with high volume potential; 2) demonstrate the benefits of sodium silicide technology in a push-to-start hydrogen release system; 3) develop a demonstration system capable of ~250 W for applications such as battery rechargers, remote telecommunications, emergency responders, backup power, and personal mobility, i.e., scooter, bicycle, etc.; and 4) improve hydrogen yield and maximize water utilization for sodium silicide-based hydrogen release.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.8** for its relevance to DOE objectives.

- Sodium silicide technology is well matched to DOE goal of FCs for portable and back-up power applications.
- Although not directly focused on automotive transportation, the project is very relevant to the DOE objectives and will contribute to the development of niche markets for hydrogen energy technologies.
- The project uses a hydrogen source that is suitable for portable and stationary FC systems.
- This project is an example of an "off-board" regenerationable chemical hydrogen storage that releases diatomic hydrogen by hydrolysis of sodium silicide and similar compounds via an exothermic reaction. It offers the ability of using interchangeable "containers" for near-term applications of moderate power, i.e., < 1,000 W).
- Hydrogen release is irreversible, so this technology is not suitable for vehicles and will not meet vehicular targets.
- The project is not relevant to automotive FC application.
- The project is applicable to hydrogen storage for portable power and consumer electronics, but is not aligned with storage targets for automotive applications. Reviewer is not sure how FCs in portable power and consumer electronics do much toward the overall goals of reducing greenhouse gas (GHG) emissions, reducing petroleum consumption, and reducing energy use.

Question 2: Approach to performing the research and development

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

- The project has excellent and clear objectives and methodology. The work plan is focused on the objectives.
- Early stage prototypes provide opportunity to assess behavior in various demonstrations.
- The project has a well defined approach and execution.
- The approach is systematic and well developed, from concept development to hardware development and testing.
- The project adresses the barrier of power density for consumer electronics, and has also addressed system issues and start-stop issues.
- The approach to the project is methodical and designed to address technical barriers, except for the cost issue that was absent this time (and was present in 2009).

- The presentation is more like a marketing document than technical summary of issues being addressed to improved capability and performance of this storage system.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.3** based on accomplishments.

- Excellent progress has been made with an eye toward commercialization; the work has been field tested.
- The project has developed and fabricated prototype storage devices for operating FC power units.
- Investigators have developed and tested a number of small to large demonstration systems. Investigators have clearly demonstrated a suitable technology for an early FC market.
- A hydrogen release system was developed, tested, and verified. No adverse issues were identified.
- The project has developed a chemistry and designed a delivery system that can provide diatomic hydrogen cheaply to portable electronics.
- The pace of progress seems good for the length of time since the project's inception. The second generation prototype seems ready for ramping up to first scale production quantities. The remaining time to the project's conclusion in 2011 seems reasonable, as long as production commences soon. The project has focused good attention to FC performance needs.
- It is not clear what level of materials assessment has been done in this project, which has a substantial amount of DOE funding (more than $2.4 million in 2 years).
- There does not appear to be any efforts taken to address energy and cost requirements to regenerate spent fuel.
- Potential safety issues with excessive temperatures or pressure generation during the hydrolysis reaction in the storage bed seemed not to have been considered in sufficient detail.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- There is a good collaboration with an FC partner, Trulite. The "back and forth" during development seems to have led to a robust prototype.
- SiGNa Chemistry has two subcontractors who are apparently making useful contributions. There are nice collaborations with industry and universities.
- There are good collaborations with Trulite Inc. and the University of Texas at Austin.
- The project team is collaborating with TruLite.
- Collaborations with a personal computer (PC) maker or electronics maker would be good (such as Dell, Apple, Samsung, Sony, Motorola, etc.).
- The depth of collaboration with the University of Texas did not come out in the presentation nor in discussion.
- There does not appear to be any formal or informal interactions with other organizations involved in chemical hydrides or metal hydrides.

Question 5: Approach to and relevance of proposed future research

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

- There is a good focus on improvement, validation, and technology transfer.
- A general plan for improving design of storage system and material properties to increase storage capacity is reasonable. However, there was little insight into how SiGNa Chemistry intends to accomplish this.
- Investigators have a clear plan to improve hydrogen yield and reduce water requirement.
- Proposed future work is sound. This project will conclude in 6 months.
- Plans to look at higher diatomic hydrogen density materials are scheduled. The project team should look some at the recovery of spent material, and the comparisons of the environmental impacts of disposal of the canister versus battery disposal.
- A 9.8% pure material hydrogen content is relatively low, and even lower relative to entire system. Reducing the excess water needs are still an important objective to address.

Strengths and weaknesses

Strengths

- Although not directly focused on automotive transportation, the project is very relevant to the DOE objectives and will contribute to the development of niche markets for hydrogen energy technologies.
- This project takes a feasible chemical storage approach using hydrolysis of silicides to release hydrogen.
- Fabrication and operation of prototypes should lead to advances in system designs and optimization.
- Investigators have demonstrated a low weight, high purity, and controllable hydrogen source for portable and stationary FCs.
- The project team has excellent technical experience.
- The project pursues high energy density storage that beats batteries with a low cost.
- Their project team made a good choice for a hydrogen storage media. The hydrogen release dynamics seem well fitted to FCs and ultimate application characteristics. The disposal of spent cartridges does not appear to create undo issues. The project has applied good technical resources to the effort.

Weaknesses

- The estimation of overall energy efficiency (although this is not critical for the likely niche applications of this technology).
- The current prototypes seem to have gravimetric capacities of no more that 2-3 percent weight (wt%), which is well below the DOE targets for vehicles, although probably sufficient for other early market applications.
- Control of reaction temperature and pressure during reaction seems difficult using the simple pumping of water into the storage container.
- The costs of the complete storage systems seem to be rather optimistic.
- Little or no attention was given to what to do with the vessels with spent fuel or how to regenerate the decomposition products.
- The primary concern is with what to do with the used canisters in the larger (stationary) systems. The final product has a very high pH and could be dangerous if exposed. More safety tests are clearly needed to ensure the canisters are safe.
- It is not really clear what will happen to the material in the larger canisters after it is used (presumably the smaller canisters will be thrown away). What type of recycling program will be used?
- Not applicable to automotive application.
- Waste product is corrosive—high pH material.
- No weaknesses evident.

Specific recommendations and additions or deletions to the work scope

- I recommend more attention be given to safety issues of the vessel along with handling and processing of the spent fuel.
- More safety tests are clearly needed to ensure the canisters are safe especially after releasing hydrogen.
- It may be worthwhile to consider a recycling program for the larger canisters.
- It would be good to have information on system pricing estimate. Ultimate commercialization depends on performance, acceptance, and pricing, among other things.
- It would be good to have information on performance data for an FC when coupled to load and to discover how an FC plus application performs under real life conditions.

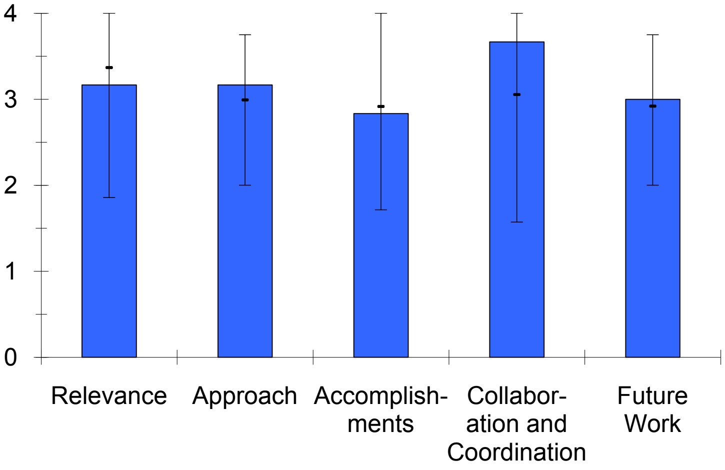
Project # ST-92: SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence: Design and Testing of Metal Hydride and Adsorbent Systems

Ted Motyka; Savannah River National Laboratory

Brief Summary of Project

The objectives of this project are to: 1) collect media property data for metal hydrides (MHs) and adsorbents, 2) collect operational data for storage systems, 3) develop a general format for models, and 4) develop an "acceptability envelope" of media characteristics based on 2010 and 2015 DOE technical targets.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- The objective of this project is significantly important to investigate system utilized hydrogen storage materials.
- This project by the Savannah River National Laboratory (SRNL) is their technical contribution to the Hydrogen Storage Engineering Center of Excellence (Engineering CoE), which mainly addresses the behavior of metal hydrides and carbon adsorbents. All of the performance issues necessary for optimizing storage potential for these materials are being addressed for the candidate materials sodium aluminum hydride and activated carbon.
- This project is consistent with the objectives of the Hydrogen Program and fully supports DOE research, development and demonstration (RD&D) objectives.
- The overall relevance of the project aligns well with Hydrogen Program objectives, assuming that the Materials CoE can continue to support the program.
- This project addresses the prototype system requirements for materials-based hydrogen storage systems. It is crucial for the transition of such systems to actual vehicular applications.
- Since there are no metal hydrides or otherwise hydrogen storage materials that meet DOE hydrogen storage material targets, there is no real justification for conducting this work with the objectives given here. DOE funds are better spent on supporting smaller projects that address material level problems–instead of conducting a hypothetical system-level optimization effort like this one.

Question 2: Approach to performing the research and development

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

- The presentation clearly shows the methodology to reach the goal.
- The SRNL project is closely integrated within the Engineering CoE to address the issues needed to improved storage behavior of metal hydrides and carbon sorbents. Essentially all critical barriers are being addressed, although they cannot be met with the available candidate materials. However, the concepts and methodology should be applicable to other materials with hopefully better intrinsic properties.
- Selection of near- and mid-term MH candidates for engineering development is sound.
- Compiling metal and adsorption hydride data is critical to modeling efforts.
- Developing an "acceptability envelope" of hydride properties provides a great pathway for the downselection of materials.
- The perception is that some of the tasks defined in this project may be redundant when compared with those of other Engineering CoE participants.

- The "acceptability envelope" is an excellent methodology for the optimum up-selection of MH and adsorbent materials at the end of Phase 1.
- The PI's approach lacks the core premise of having a viable hydrogen storage material at hand. Without a good MH based diatomic hydrogen storage material, the approach proposed is of little relevance.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- At present, looking from the "spider chart," there is no appropriate material to meet any DOE system targets. There are no tactics to find out candidate(s) of media for prototype testing.
- Substantial amounts of materials properties have been gathered and assessed for several candidate storage materials and these results were incorporated into detailed thermal performance models. Predictions were compared with literature bed configurations and laboratory testing data. Requirements for hydride and adsorbent beds were developed. It was shown that current candidates are unlikely to meet DOE targets.
- Resources devoted to sodium aluminum hydride may be wasted since sodium aluminum hydride has no chance of becoming a viable diatomic hydrogen carrier due to very low system capacities that will not meet DOE targets.
- Development of the kinetics, heat, and mass transfer models are on target.
- Progress on technical accomplishments appears to be on track; however, no detailed schedule was provided. The "refined" model for a physisorption storage system needs further improvement when compared with the measured thermal profiles.
- A great deal of progress has been made.
- It is unclear what is being done to address the sodium aluminum hydride system shortfall issues associated with gravimetric density, cycle life, safety, and toxicity.
- The objective of building databases for the failed diatomic hydrogen storage materials: sodium aluminum hydride, lithium amide, magnesium hydride, titanium chromium manganese, or the magnesium alloy Mg_2Ni is not clear. Building databases for compounds has definite value, but is not necessary for this work. A good deal of sophisticated computational fluid dynamics (CFD) and heat transfer modeling is in progress, but their value to the development of a system level hydrogen storage system (that meets DOE targets) from the currently less-than-adequate hydrogen storage materials is not known. For the sodium aluminum hydride that was analyzed as an example of the accomplishments in the present report, researchers point out that 17 DOE targets were achieved and 4 (excluding costs) were not! This reviewer is uncertain of the reason to spend so much money and effort if the result is already predictable and well known. Of course, sodium aluminum hydride cannot meet system-level DOE targets for the gravimetric density, cycle life, etc., because the sodium aluminum material fails those requirements! Furthermore, the arbitrary target of minimum required diatomic hydrogen percent weight (wt%) stored in the material to meet 40% of the DOE 2010 gravimetric density requirement (assuming a 50:50 material to system gravimetric ratio) does not make any sense at all.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.7** for technology transfer and collaboration.

- A wide variety of world class experts contributed to the project. In addition, they seem to collaborate closely.
- SRNL has involved many of its Engineering CoE partners in this effort, which resulted in highly coordinated assessments. SRNL also worked closely with several partners from the hydride and sorbent CoEs.
- There are excellent collaborations among the many Engineering CoE partners.
- A very capable team has been established.
- There is an excellent collection of partners. The project appears to be well coordinated.
- There are many entities involved–perhaps too many.

Question 5: Approach to and relevance of proposed future research

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

- The role of this CoE is not to develop materials, but to conduct engineering research. This project contains only an evaluation of the media. There must be an option to continue material research even under the Engineering CoE, and this project seems to be an appropriate umbrella for material research.
- SRNL has outlined a comprehensive list of fiscal year FY 10 and FY 11 activities to support the Engineering CoE Phase 1 go/no-go review. Alternative candidates and bed configuration will be assessed using the methodology and simulation models developed during the past year. Presumably all DOE system targets will be addressed.
- Proposed future work is very good.
- There is a need to establish a clearly defined test matrix of candidate storage materials based upon the Materials CoE recommendations.
- Future work addresses the key areas.
- The project team should quit building a database of inadequate hydrogen storage materials.
- The project team should provide justification for why it is necessary to develop detailed models to compare storage system behavior for different media (metal hydrides, metal organic framework- (MOF-5) and AX-21) – none of which is acceptable hydrogen storage medium.
- The project team should add cost considerations.

Strengths and weaknesses

Strengths

- They have a clear methodology and a significant number of world-class experts in materials.
- SRNL has established an extensive materials property database to analyze and predict the behavior of storage systems based upon hydrides and adsorbents. This is a well-balanced package of numerical modeling methods with detailed integration of relevant materials properties.
- The project team has strong collaborations.
- The partners have an excellent understanding of the technical work.
- The project has a well defined architecture in the modeling hierarchy toward addressing the Engineering CoE goals.
- This is a very strong team contributing to the project.
- Successful completion of model development will establish the theoretical boundaries of expected performance from any given storage system design and storage media.
- Excellent team. Excellent approach.
- Researchers and scientists involved in this Engineering CoE are capable individuals in their respective fields.

Weaknesses

- The major task is collection and evaluation of material data that have already existed. It is unclear how the risk of not finding an appropriate material will be eliminated.
- The most complete information available for evaluation is for materials that cannot meet the system targets for hydrogen storage materials. Hence, optimization procedures may not correctly identify more effective design/material combinations.
- None.
- Project activities have a high potential for replication of effort, past and present.
- While no detailed schedule of project tasks was given, the success of the project is likely to be constrained by time unless media property data become available very early in the project schedule.
- Software models and hardware designs are based on yet-to-be-discovered hydrogen storage materials with unknown characteristics and thermophysical properties. The lack of cost considerations is a real weakness.

Specific recommendations and additions or deletions to the work scope

- This project needs collaboration with materials research. The results of this study under this project should reflect to the material investigation. Feedback from this project is definitely useful for development of advanced materials.

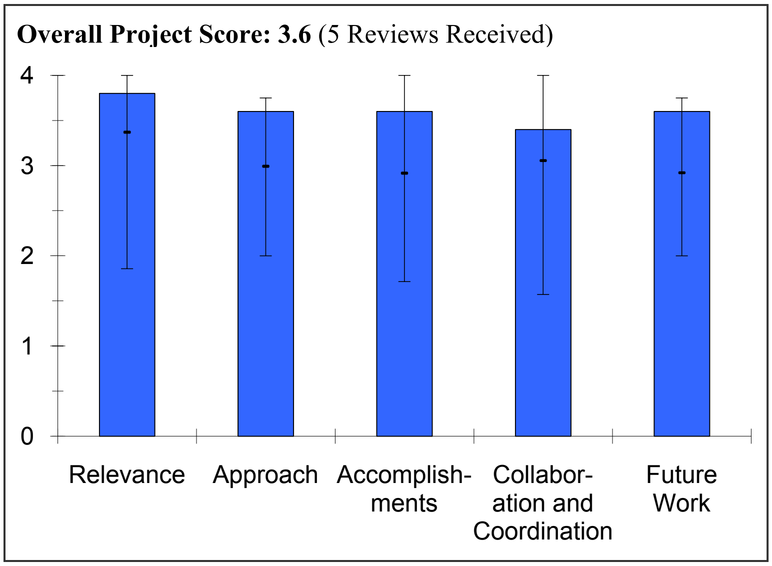
- There are none beyond those outlined on slide 24 of the SRNL AMR poster.
- Other materials based on the Materials CoE recommendations need to be considered.
- The scope of work needs substantial modification and roll back.

Project # ST-93: High Strength Carbon Fibers

Felix Paulauskas; Oak Ridge National Laboratory

Brief Summary of Project

The overall objective of this project is to reduce the manufacturing cost of high strength carbon fibers (CF) by means of: 1) significant reduction in the production cost of the polyacrylonitrile (PAN)-precursor via hot melt methodology; and 2) later on, the application of advance carbon fiber conversion technologies development at the Oak Ridge National Laboratory (ORNL).



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.8** for its relevance to DOE objectives.

- Extremely high—all storage systems, with the exception of some chemical hydrogen storage materials, will need cost effective pressurized storage tanks. The CF is currently the largest contributor to cost of those systems. It is essential to find low-cost fiber options that will allow the supply to meet the demand of such high strength fibers
- This project is significantly important to reduce the cost of CF that is indispensable for high pressure hydrogen cylinder.
- This project aims to reduce the cost of CFs that are needed for super reinforced tanks for high pressure hydrogen. If successful, this project would have a significant impact on the cost of hydrogen based alternative energy systems.
- High strength fiber is critical for high pressure hydrogen storage tanks.
- This project is important for the commercial success of the hydrogen economy. It is clear the most significant cost driver of a compressed fuel system is the hydrogen tank, and the cost driver of the hydrogen tank is the CF.
- This project is essential to reduce the cost of CFs and to advance the development of CF manufacturing.
- In my opinion, this project is underfunded and needs more support based on the high relevance to the hydrogen program.

Question 2: Approach to performing the research and development

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

- The PI is working on the process to simplify and eliminate impurities (largest contributor to fiber strength and yield).
- The approach to reach the goal is clear, and, if successful, it will provide a novel and less expensive way to produce high strength CF.
- This project involves improving a melt spinning approach to fiber synthesis as a low-cost alternative to conventional preparation techniques. This seems like a very good direction to go in the area of structural CF production.
- Replacing the wet spinning with melt spinning may provide a cost effective way to achieve large scale production of fibers.
- The approach is excellent based on the limited level of funding. The project has a good focus from a manufacturing viewpoint. In future presentations, the results of the fiber attributes, i.e., variability and performance, should be provided in comparison to the goals.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.6** based on accomplishments.

- The PI is making fantastic progress despite the extremely limited funds.
- With only 2 years R&D, great progress has been made, but it is still not satisfactory to apply to real products.
- Progress has been made in the synthesis of long fibers using the melt spinning technique. Additional advances are needed to demonstrate viability of production, especially process efficiency and scalability.
- The program appears to be on schedule.
- The accomplishments for the past year have made a significant step toward realizing the feasibility of the melt spun process. It was nice to see the example of the filament manufactured from the PAN-melt spinning process at the AMR.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- DOE should continue and strengthen collaboration and funding of this project with the FreedomCAR Materials Technical Team (MTT) or US Automotive Materials Partnership (USAMP). Clearly the benefits of this project apply to those teams as well. The PI is leveraging the laboratory facilities with a current MTT project, but needs more people and funding to address the different program goals and intent, i.e., different fiber quality and strength.
- Such coordination could also help achieve a competitively bid status with this project.
- It seems to be difficult to find good collaborator(s) in the United States because high strength CF is produced only in Japan at present.
- This project incorporates several collaborators who bring much needed expertise to bear on the objectives of the work.
- This project has reasonable collaborations.
- The collaboration of partners seems to be well organized and appears to have the correct leaders in the field. In the future, it would be useful to have feedback from the industry producers to ensure the process steps can be scaled and transferred to a large-scale industrial setting.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.6** for proposed future work.

- The PI is continuing efforts, but is hampered by the budget and lack of staff. This reviewer strongly urges DOE to increase funding for this project and the pace. The payback for this project for many industries and sectors will be many fold the investment.
- When IP is locked in, the PI needs to reveal the source of the “holy water.”
- The plan is very clear.
- The next steps in the project are clearly indicated.
- The description of future work is vague and difficult to evaluate.
- The general future work is consistent with project goals. In the future, further detailed next steps would be appropriate to understand the items in the process that could be modified and the predicted levels of improvement in order to achieve an acceptable hot-melt PAN filament/tows.

Strengths and weaknesses

Strengths

- Reasonably-priced high strength CF is produced using unique idea from ORNL.
- Development in this area of high strength and low cost CFs is essential to commercialization of high pressure hydrogen storage tanks, plus there are many other applications. This is important work.
- There is the potential for low cost fiber production.
- There is high alignment to the cost issue associated with the hydrogen fuel system.

Weaknesses
- Collaboration with industry seems to be weak. It may be the time to start close collaboration with industry.
- This is an unusual project since the primary goal is cost reduction. Technical weaknesses, if any, are nearly impossible to estimate.
- As the project proceeds, fiber attributes should be provided.

Specific recommendations and additions or deletions to the work scope

- Collaboration with industry is strongly recommended.
- Additional funding is needed for this important project.
- Further scope should include fiber performance in a matrix structure; i.e., evaluate translation strength.

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