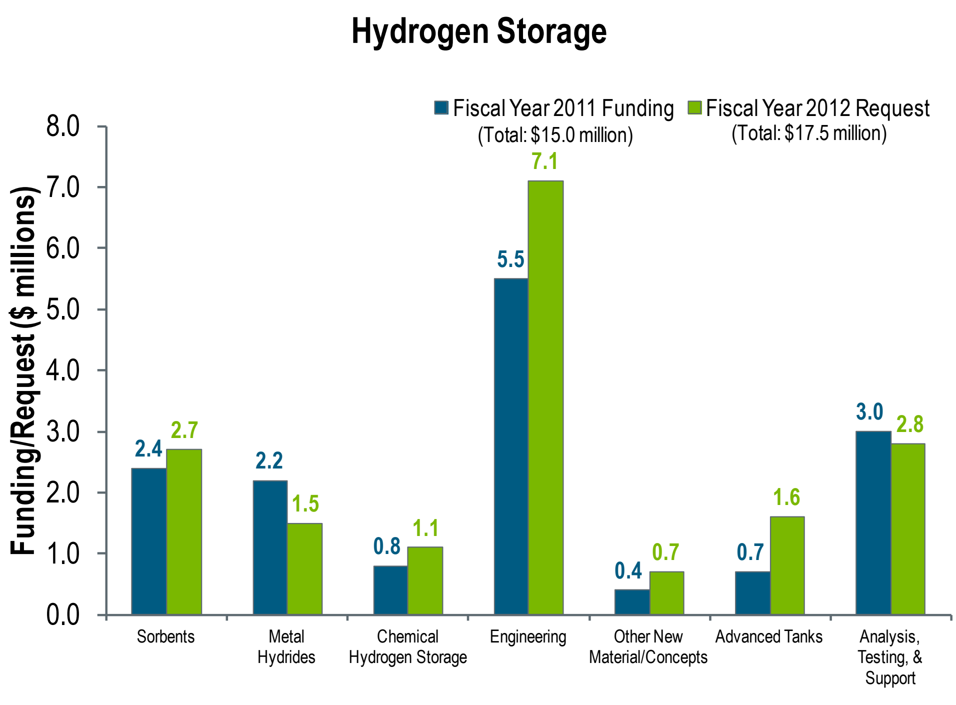
2011 — Hydrogen Storage
Summary of Annual Merit Review of the Hydrogen Storage Sub-Program

Summary of Reviewer Comments on Hydrogen Storage Sub-Program:

The Hydrogen Storage sub-program portfolio remained focused in fiscal year (FY) 2011 on materials-based research and development (R&D) and expanded efforts in system engineering for onboard transportation applications. In addition, in FY 2011 more efforts have been directed at reducing the cost of compressed gas storage systems for near-term applications. Reviewers observed that the sub-program's 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. They also supported the sub-program's additional emphasis on physical storage (e.g., compressed hydrogen gas) for nearer-term applications. Reviewers stated that good progress has been demonstrated through the Hydrogen Storage sub-program activities. Overall, reviewers commented that the sub-program appears well managed and well organized, and they found it to be flexible in its ability to make shifts in strategy to accommodate changes in program priorities and funding.

Hydrogen Storage Funding by Technology:

The chart below illustrates the appropriated funding in FY 2011 and the FY 2012 request for each major activity. In FY 2011, the sub-program received $15 million in funding, with a request of $17.5 million for FY 2012. The Hydrogen Storage Engineering Center of Excellence (HSECoE) continues to be a major activity for the sub-program, as does the continuation of new materials development for hydrogen storage. Work directed at lowering the cost of compressed gas storage for near-term commercialization will also receive increased effort in the coming year.



Majority of Reviewer Comments and Recommendations:

The Storage portfolio was represented by 31 oral and 16 poster presentations in 2011. A total of 37 projects (29 presentations and 8 posters) were reviewed. In general, the reviewer scores for the storage projects were good, with scores of 3.5, 3.0, and 1.5 for the highest, average, and lowest scores, respectively.

Chemical Hydrogen Storage: Two projects on development of chemical hydrogen storage materials were reviewed, with an average score of 3.0. In general, the reviewers were complimentary of the work being performed and the progress being made. The combined use of computational and experimental efforts was lauded by reviewers. While reviewers were encouraged by the relatively low heats of adsorption, they expressed concerns over the relatively low hydrogen capacity by weight and need for high amounts of desorption catalysts for the boron- and nitrogen-substituted carbon heterocycle materials.

Advanced Metal Hydrides: Seven advanced metal hydride projects were reviewed, scoring a high of 3.5 and a low of 2.9, with an average score of 3.2. In general, the reviewers found the advanced metal hydride activities to be very relevant to the sub-program's objectives, and they felt that barriers—e.g., kinetics, gravimetric capacity, and thermodynamics—were being addressed. Much of the work was considered innovative and promising results have been obtained, such as demonstrating more than 12 weight percent for magnesium borohydride ($Mg(BH_4)_2$) and high desorption kinetics for 60% mass-loaded slurries of alane (AlH_3). However, some concerns were raised, such as many materials do not have sufficiently high capacities to be able to meet the storage system targets, and kinetics are still too slow at the target temperatures. Many of the advanced metal hydride projects are in the final project stages and are scheduled to end within the next year or so.

Sorbent Materials: Seven sorbent projects were reviewed, with an average score of 3.0. Overall, the reviewers found the sorbent work to be highly relevant to the sub-program's objectives. Much of the work was thought to be well planned and well executed. In general, the reviewers were appreciative of the efforts to increase the capacity of many of the sorbent materials through development of materials with increased surface area. However, the reviewers were less convinced that through this approach materials capable of meeting the volumetric target could be developed or that the addition of metal species will sufficiently alter binding energy to allow significant adsorption above cryogenic temperatures. Of specific interest was the effort to validate whether the spillover phenomena led to enhanced adsorption capacity at room temperature. Reviewers commented that this is a critical activity for the U.S. Department of Energy (DOE) and praised the strong international team assembled for the effort. Reviewers expressed concern regarding some delays that have occurred and, in particular, regarding how these delays would affect the projects' abilities to meet the stated objectives within the remaining time planned for the effort.

Engineering: For the HSECoE, 11 projects were reviewed, with an average of 3.1. The reviewers found management of the HSECoE to be well coordinated and well structured. The reviewers did note the difficulty of managing a team of 10 partners covering the range and complexity of engineering complete materials-based storage systems for each of three materials classes—sorbents, reversible metal hydrides, and chemical hydrogen storage materials. The reviewers also noted that no current existing storage material possesses all the requisite properties for a system to meet all DOE performance targets for onboard storage systems; however, they accepted the HSECoE's approach of using surrogate materials and identifying and addressing the key technical barriers. As for the individual partner reviews, in general, the partner plans and work efforts were thought to be appropriate and well performed. Reviewers expressed concern over coordination of the various teams and the potential for overlap of efforts and delays in required activities. In general, it was thought that good progress has been made by the HSECoE partners in evaluating and identifying technology gaps in the ability of materials-based systems to meet DOE performance targets. Concern was raised over the potential difficulty in translating the results obtained for surrogate materials to materials of choice once they are identified.

Advanced Tanks: Two projects related to advanced tanks were reviewed, with an average score of 3.1. The reviewers considered these two efforts to be of high value to the sub-program and stated that they addressed critical areas. With the initial commercialization of hydrogen-fueled vehicles expected to use high-pressure composite cylinders for compressed gas storage, they observed that understanding hydrogen permeation through the liner materials and lowering the cost to produce the cylinders are critical efforts for DOE to fund. Reviewers would like to see more collaboration on both projects, especially with industry.

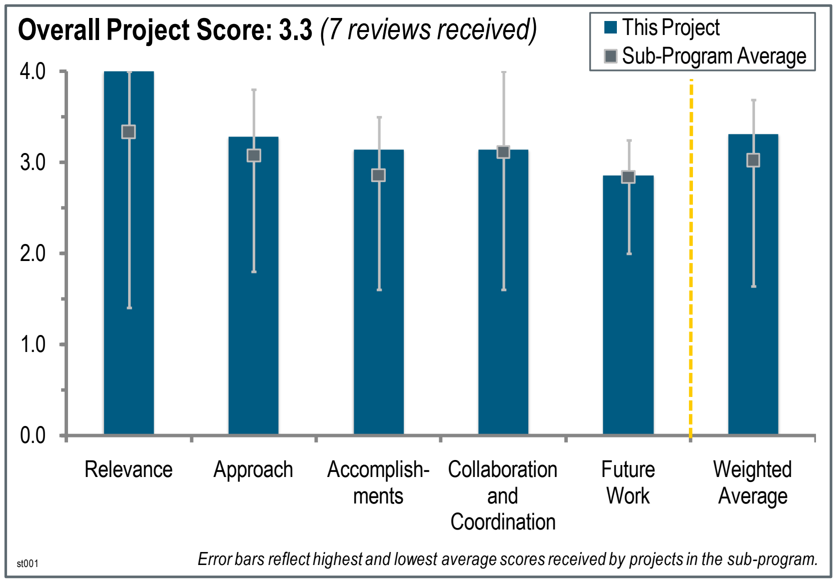
Analysis, Testing, and Support: Six projects were reviewed in the Analysis, Testing, and Support category, with an average score of 3.1. The Analysis, Testing, and Support efforts cover a breadth of activities in support of the Hydrogen Storage sub-program and provide independent verification of the potential of the various materials and technologies being developed through the sub-program. In general, the reviewers considered these efforts to be highly relevant and critical. The system and cost analysis activities were found to be effective, with good progress being made. The development of the "Best Practices" reference guide was thought to serve an important role by providing a standard basis for researchers to use in their testing and evaluation of hydrogen storage materials. The inclusion of international collaborators in providing input to and review of the documents was thought be an excellent contribution. Two new efforts were initiated by the DOE this year to review and identify key near-term hydrogen fuel cell markets where hydrogen storage is a barrier to commercialization. The reviewers lauded the strong collaboration between the two projects, but expressed concern over the limited apparent stakeholder input the projects had received to date.

Project # ST-001: System Level Analysis of Hydrogen Storage Options

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project:

The objectives of this project are to: (1) conduct independent systems analysis for the U.S. Department of Energy (DOE) to gauge the performance of hydrogen storage systems; (2) provide results to material developers for assessment against performance targets and goals, and help them focus on areas requiring improvements; (3) provide inputs for independent analysis of the costs of onboard systems; (4) identify interface issues and opportunities, and data needs for technology development; and (5) perform reverse engineering to define material properties needed to meet the system level targets.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **4.0** for its relevance to DOE objectives.

- Argonne National Laboratory (ANL) is providing high-quality systems analyses to support hydrogen storage projects with respect to the assessment of various storage approaches compared to performance targets for light-duty vehicles. ANL's results provide important insights on the attributes and limitations of current configurations toward meeting technical and cost goals. This information has been very useful for making go/no-go decisions on continuing storage development projects as well as providing independent insight on the progress and potential of these storage systems.
- This project fully supports DOE's research, development, and demonstration objectives. The results of the system analysis work create a solid foundation for a comprehensive and quantitative assessment of different hydrogen storage system options. This information is critical for assessing the viability of candidate systems for vehicular transport applications and for establishing future directions for hydrogen storage and fuel cell development and engineering activities.
- Independent analysis is very important. This project provided useful information to other projects. One example is the suggestion to Los Alamos National Laboratory (LANL) about the regeneration process of ammonia borane, which was extremely valuable to development of an energy efficient regeneration process.
- This project is highly relevant to DOE objectives as it provides practical engineering assessments of selected systems being investigated in the DOE Hydrogen and Fuel Cells Program.
- This is a highly relevant project that is crucial to the success of the Program.
- The development of system models to evaluate status and research needs is highly relevant for supporting Program objectives.
- This is a very relevant project.

Question 2: Approach to performing the work

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

- 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 onboard and off-board refueling performance targets. ANL collects and updates inputs from various sources to obtain reasonably complete descriptions of hydrogen storage systems, and its 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, such as reliable reaction rates for hydrogen reaction with the storage media in the appropriate operating temperatures, or important thermophysical parameters, such as thermal conductance of powders or compacted sorbents. The consistent application of tradeoff studies to determine the influence of various parameters is also valuable to identify which have the most impact on achieving or limiting the performance targets.

- A comprehensive and systematic technical approach has been adopted. Straightforward thermodynamic and kinetic models are used to analyze the behavior of three distinctly different storage systems and to provide a solid basis for understanding the trade-offs of those candidate materials in a practical storage and delivery system.
- The approach used by the ANL team addresses the main issues that are critical to achieving system goals (i.e., capacity, charge and discharge rates, efficiencies, and cost), and it has conducted trade-off analyses that are helping to resolve system-level issues associated with the different material options.
- The approach also includes productive collaborations with the Hydrogen Storage Engineering Center of Excellence (HSECoE) and Storage System Analysis Working Group (SSAWG). These are essential to ensuring the transfer of system analysis work to organizations focused on engineering development.
- An ongoing concern is that the termination of the three materials centers of excellence means that the flow of new materials to this project will be limited. Although this is not a criticism of the ANL effort, it could nonetheless diminish the overall impact of the project.
- The approach is appropriate and the analyses focus on specific systems. The aim of this project is to provide information to materials developers, not system engineers. Considering the near end-of-project status of the materials-based Centers of Excellence (CoE), and the aim of the project, it is acceptable.
- The general approach of using thermodynamic and kinetic models is very good at providing the functional assessment of the hydrogen storage systems. The selection of certain design approaches could be further justified. For example, the adiabatic cooling approach for the metal-organic framework (MOF) could have included a forecourt assessment to explain the reason for evaluating this concept versus station cooling. Other choices in system design assumptions should be fully explained.
- The researchers seem to have achieved some good work overall, but it is difficult to evaluate the project properly with the information given. The results are interesting, but they should be validated experimentally and more details about the modeling strategies should be provided. More details about the MOF-5 isotherms used to parameterize the adsorption model should be provided, such as:
    - Who measured the isotherms
    - Whether they were from a single source (the 83 kelvin [K] and the 77 K seemed to come from two sources)
    - What the model parameters were
    - Whether the differential energy of adsorption was derived from the isotherm or fitted to a constant
- The analysis approach is very good and reasonably believable in the absence of prototype construction and testing. Although the storage methods analyzed are more or less self-evident in covering a spectrum of options, it is not fully clear why all of the examples were chosen. This reviewer asks if they were requested by DOE or if they resulted from interactions among DOE, ANL, and principal investigators (advocates).

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- Good progress has been made in 2010 and 2011 on analysis and evaluation of four important storage approaches. These analyses have allowed a meaningful comparison of performance and cost metrics for each approach with DOE targets for onboard storage. The ANL team has addressed critical issues and system trade-offs in a straightforward and comprehensive way. The information provided in these studies will be critical to making sound and well reasoned decisions on the final selection and validation of storage materials and system approaches.
- One concern is that only limited information is provided concerning the remaining areas of risk as well as challenges that must be addressed for each of the candidate systems. Likewise, a detailed risk mitigation strategy is not evident from the material presented here. A candid statement of risk areas, potential "showstoppers," and potential ways to mitigate risk in each technology area would be helpful.

- This project has generated much valuable information that will help guide future "go/no-go" funding decisions by DOE. The works on MOF-5 and alane systems are nicely detailed. The relatively low efficiency and the generation of greenhouse gases (GHG) during ammonia borane (AB) regeneration give pause. Based on the project results, it would seem that all the DOE targets cannot likely be met for some time, if ever. This reviewer wonders if this suggests that the DOE targets need to be rethought.
- The greatest efforts during the past year were in updating assessments of physical storage systems, adsorption by powder and compacted MOF-5 adsorbents, and the AB/ionic liquid (IL) and alane slurry chemical storage systems. The researchers' analysis indicates that all of the materials-based approaches for hydrogen storage still have serious limitations. For example, except for having slightly better dormancy properties, their analyses of the MOF-5 options show lower capacities than previously evaluated cryo-compressed storage vessels. All analyses of the MOF systems have considered only refueling with liquid hydrogen, which reduces overall efficiency, while others (i.e., the HSECoE team) are using liquid nitrogen cooling during refueling. Their assessments on the off-board performance of AB/IL and alane chemical storage systems point out severe issues (especially with the hydrazine regeneration of AB) with wheel-to-tank efficiencies. Once again, the ANL team has investigated a broad range of systems in considerable depth.
- The project has shown good progress in hydrogen storage system analysis.
- The results of the analysis are informative.

Question 4: Collaboration and coordination with other institutions

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

- Extensive and valuable collaborations exist among the ANL SSAWG team, HSECoE partners, and external organizations. Previous collaborations with the materials-based CoEs were important in the selection of the best candidate materials for study. The TIAX collaboration has been especially important. There is a clearly defined division of effort among the partners, and the overall project is well managed and coordinated.
- The collaborations are numerous and excellent at all levels. ANL should be a valuable member of SSAWG.
- ANL worked with TIAX in predicting both onboard and off-board costs for several storage systems. There were close interactions and exchanges of technical information with a number of other organizations, including Lawrence Livermore National Laboratory, Brookhaven National Laboratory (BNL), LANL, Ford, and BMW. While there has been some cooperation with the HSECoE during the past year, this reviewer feels that more sharing and direct comparisons of modeling efforts would be beneficial both to avoid any redundancy and to compare results and conclusions.
- The project collaboration with industry, national laboratories, and the HSECoE is very good and needs to be maintained to ensure the project aligns with the current state of hydrogen storage technologies. Further coordination with the HSECoE should be encouraged to avoid redundancy and appropriate synergy.
- This project provides an important counterweight and check to the analysis work being done in the HSECoE.
- Even though there is some duplication between these two efforts, it is advantageous to have them both as part of the DOE portfolio. The project only addresses the materials-based CoEs, which are not expected to be operating in the near future. This reviewer does not understand the collaboration between this project and the HSECoE.
- It is unclear how this project relates to the ongoing work being performed at the HSECoE.

Question 5: Proposed future work

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

- Further comprehensive analyses of the compressed and cryo-compressed storage vessels that include variations in design configurations and optimization that address manufacturing constraints for safety and structural materials (e.g., carbon fibers and aluminum versus stainless steel) is fully supported. Performance analyses of the alane slurry system should only be done assuming the updated kinetics and composition results from BNL indicate higher performance potential. Unless a much more efficient AB regeneration scheme can be identified with waste-to-energy values of greater than approximately 40%, there does not seem to be a need for further onboard and off-board assessments of the AB/IL storage system.
- The future work is a straightforward extension of the work conducted in 2010 and 2011; however, the future work statement is very general. Because obstacles, challenges, and potential roadblocks have not been clearly

articulated, the future work lacks a proper context. For example, the remaining problems to be explored and exactly how will they be addressed are unclear. A more clearly defined statement of specific issues and plans would be helpful. Reverse engineering to define material properties needed to meet targets was proposed in the 2011 presentation; however, no mention of that approach is given in the future work statement. This reviewer wonders if that is still considered to be an important part of the overall plan.

- The future work appears to build on past progress and is focused on the needed hydrogen storage areas of development. It would be helpful to provide further details on the plans for future work and provide specific information regarding the key differences from the previous analysis.
- The proposed questions to be answered are reasonable. If the regeneration of AB is so poor from efficiency and GHG considerations, at least in comparison to alternatives in slide 21, this reviewer wonders if future activities on this approach should be shelved until a significantly better regeneration process is developed.
- Much closer collaboration with the HSECoE is expected.

Project strengths:

- This project is one of the key projects in the Program. It has proved significantly informative to the material developers. There is also collaboration with many institutions, and collecting appropriate data is a strong point of this project.
- ANL has developed very comprehensive analytical tools for detailed engineering assessment of both the onboard and off-board aspects of hydrogen storage. Its results appear to be very reliable and robust compared to current knowledge and the experience of others with available prototype and demonstration storage systems. The engineering staff at ANL provided clear presentations of their methods and results. Analyses appear to be based on best available data from various sources.
- This is a well managed technical effort conducted by a strong team with considerable expertise and background in hydrogen storage system modeling and trade-off analysis. This project directly complements and supports related activities in the HSECoE, and it is making important contributions to the design and implementation of an onboard storage and delivery system that meets the DOE goals.
- System analysis is very valuable to DOE decision-making.
- The project provides a very good assessment of hydrogen storage systems and provides a comprehensive comparison to the key DOE targets. The project involves a single source for assessing the various storage systems that has a good knowledge of the overall fuel cell integration.

Project weaknesses:

- A clear statement of remaining issues, obstacles, and risk areas is needed. This will provide a better basis for developing and executing a better defined future work plan.
- This project aims to provide information to the material developers, even though this year's analyses have been made for systems. Collaboration with the HSECoE is strongly expected.
- The primary challenge for these analyses by ANL is the limited availability of reliable and complete reaction parameters (i.e., kinetics data) for the various hydrogen storage media over sufficiently broad temperature ranges to generate robust predictions of performance in specific designs. Without the capability of generating the necessary input parameters themselves, ANL appears to sometimes extrapolate properties outside of reasonable limits and may not be capable of fully establishing the correct behavior.
- There are really no weaknesses. Conclusions should perhaps be more forceful in recommending no-go decisions where implied.
- On the summary graphs, the project should identify the systems that have been recently evaluated versus outdated analysis. The project should clearly identify assumptions that are approximated or need to be validated. Additional information should be provided to highlight areas that need to be improved to direct future research.

Recommendations for additions/deletions to project scope:

- Collaboration with the HSECoE should be started, and unnecessary duplication of some of the projects conducted under the HSECoE should be stopped. This project can also provide good information to HSECoE.
- It would be good to see a table of the effects of the filling scenario.

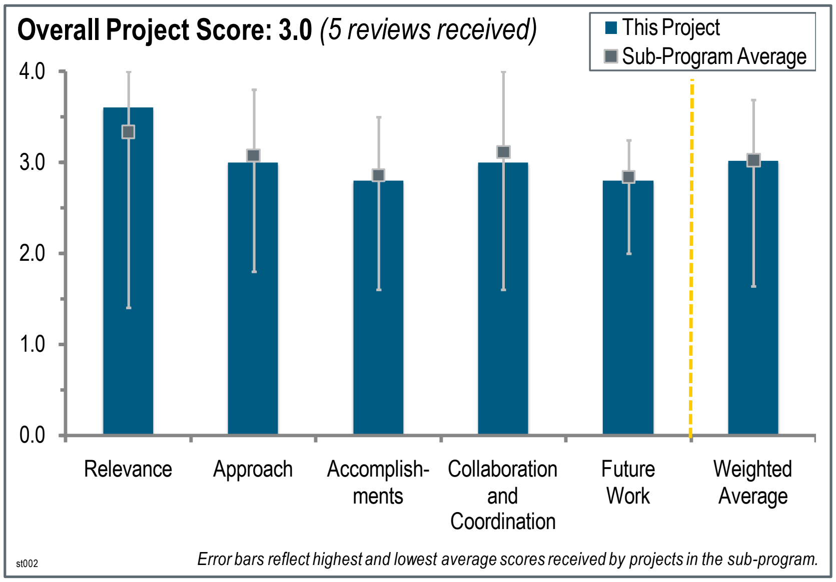
- ANL should continue to focus on comprehensive assessments of the physical storage systems in configurations that can be used in near-term vehicles and early market applications. It should also emphasize analyses to optimize the efficiency of the off-board aspects that are related to cryogenic and liquid hydrogen and the regeneration of spent fuel from the various chemical hydride storage systems. ANL probably should minimize analyses of onboard aspects of the material storage systems that are being conducted by the HSECoE. Instead, this reviewer strongly urges full and outright collaboration between ANL and the HSECoE to maximize information exchange.
- Efficient regeneration of AB, derivatives, and alane remain serious issues. Although some work was done in 2011 to evaluate selected regeneration strategies, there are still many outstanding issues that remain. For example, “one-pot” regeneration of AB from hydrazine has serious energy efficiency and cost problems. Likewise, the scale-up and efficiency of the BNL process for alane regeneration is critical to successful implementation of that approach. Sufficient work must be done so that definitive statements can be made concerning the efficiency, cost, and overall efficacy of chemical hydride regeneration approaches.
- This project should add work on classic reversible alloy hydrides for applications that are not pertinent to personal vehicle targets (e.g., forklifts). Researchers should consider interrupting work on AB regeneration until a better method is proposed, but continue to work on onboard hydrogen generation analysis.
- The project should include deliverables to connect and collaborate with the HSECoE team, as well as clear definitions of terms and assumptions along with sources of information.

Project # ST-002: Analyses of Hydrogen Storage Materials and Onboard Systems

Karen Law; TIAX, LLC

Brief Summary of Project:

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



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.6** for its relevance to DOE objectives.

- A comprehensive cost analysis is vital for selecting the best candidates and approaches for a commercially viable, hydrogen storage/delivery system for onboard transportation applications. This work is fully consistent with DOE's research, development, and demonstration objectives. The project directly supports and complements the modeling studies conducted by the Argonne National Laboratory (ANL) team and the engineering effort underway in the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- This work is critical for the goals of the DOE Hydrogen and Fuel Cells Program. While materials and engineering are also required, cost will decide the winner. For DOE to properly deploy limited funds, work of this sort is essential.
- Analysis of projected costs of hydrogen storage tanks at various production levels is very important to the Program. The project is very relevant to Program objectives, as compressed gas storage is currently the only viable means of storing hydrogen in fuel-cell-powered vehicles.
- This is a critical project.

Question 2: Approach to performing the work

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

- The approach that TIAX uses in developing cost estimates is good. It collaborated with ANL to develop the system specifications, performance parameters, and conceptual designs for the hydrogen storage systems of interest. This ensures that input from several sources is applied to the system that is costed. Capital costs are estimated by a combination of in-house models, Design for Manufacturing and Assembly analysis, and vendor quotations. Established DOE models are used to determine GHG emissions and the equivalent hydrogen selling price.
- The overall approach for the onboard cost and performance assessments relies on technology review and bottom-up cost methodologies. The approach is straightforward and effective, thereby facilitating a meaningful comparison of candidate technologies. The single-variable and multivariable sensitivity analyses provide a solid way to quantify the predicted range in the cost projections.

- The approach is adequate for a first cut, but ignores the next step of potential cost reductions at tier one, tier two, and even tier three supply chains. The project is also insufficiently grounded in data from the industries required to make the product; however, that would require a bigger effort than funded and carbon-fiber makers are notoriously tight with cost and price information.
- It is surprising to see the cost of metal-organic framework (MOF) 177 is lower than AX-21. There were not enough details in the presentation on how the pricing of the adsorbents was established. This reviewer asks if AX-21 is still available commercially.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- This project completed several physical storage system analyses. Preliminary low-volume manufacturing cost analyses were also completed. The balance of plant (BOP) component was compared with carbon fiber in terms of total cost. At a low volume, BOP is slightly more than 50%; at a high volume, carbon fiber is 80%.
- Using a single learning curve for all BOP is very risky and oversimplifies things. This rather basic approach seemed more superficial than those used in previous years, and DOE should try to discover why this is. It may be due to a change in personnel, not enough money, or a change in corporate philosophy. This should influence whether or not the researchers should get a new contract. There was good progress in 2010 and 2011 that culminated in a quantitative factory cost comparison for a number of relevant storage technologies. This is essential for assessing the commercial potential of the various approaches. The cost analyses for compressed gas systems are especially detailed and useful. However, the cost reduction predicted with the unit scale-up of compressed systems is shown to occur almost exclusively through BOP cost savings with a constant tank cost across all manufacturing volumes. That does not seem to be realistic. A more compelling case for that conclusion would have been helpful. Also, given the importance of the ammonia borane (AB)/ionic liquid (IL) system as a potential liquid carrier (currently being modeled extensively by the HSECoE), it is very surprising that a cost analysis for that system was not performed here. That is a serious omission.
- TIAX finalized high-volume factory cost estimates for compressed gas storage and for a liquid carrier system. It also finalized cost assessments for the AB first fill and regeneration process. This is a good accomplishment since the last AMR. In addition, TIAX has begun work on low-volume manufacturing costs. Weaknesses of this project include a need for a better cost model for BOP components and better estimates for non-automated process steps. In addition, the cost of inspecting fully assembled storage systems should be included.

Question 4: Collaboration and coordination with other institutions

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

- The collaboration with ANL was important. Other industrial collaborations were also important. More collaboration with component makers and materials generators (other than carbon fiber) would have improved the results.
- Collaborations are numerous and include national laboratories, tank developers, and stakeholders who reviewed assumptions and results and provided feedback and recommendations.
- This project had good collaboration and technical interchange with other organizations, especially ANL, system and equipment manufacturers, and other storage centers of excellence. However, communication between TIAX and partners in the HSECoE (especially with regard to primary model systems for engineering development) is not as evident.

Question 5: Proposed future work

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

- The proposed work is suitable, given that the project is nearly complete.
- The project has essentially ended (95% complete) and there is insufficient time to continue the technical work on this project. If a no-cost extension is adopted, the proposed plans are reasonable. In order to be relevant to the

topics currently being studied in the HSECoE, it would be helpful if the TIAX team could include at least a cursory examination of the AB/IL system.
- TIAX proposes to focus on completing low-volume cost estimates and any other analyses requested by DOE. With only 5% of the project resources remaining, not much other than the low-volume cost estimates can realistically be accomplished.

Project strengths:

- This project gives DOE the option to rate systems by cost.
- Cost analysis is a vital part of a robust commercialization strategy. The bottom-up approach and cost sensitivity analyses conducted by TIAX provides a quantitative measure of predicted costs for a wide range of relevant storage technologies. The TIAX personnel and their collaborators have extensive experience and a good track record of success.
- This project is able to perform sensitivity analyses around the most important variables. There is a good record of accomplishments over the length of the contract.

Project weaknesses:

- This project does not detail the fidelity of cost improvement by supplier improvement.
- Although it may be beyond the scope of the present project, a more detailed description of cost reduction strategies for each of the selected technologies would be useful. Also, a description of the primary risk areas and risk mitigation approaches is needed to fully assess and prioritize the different approaches. Better communication and collaboration with the HSECoE is needed.
- There is a need for a better BOP cost model, perhaps based on TIAX design and costing, for a simpler BOP system that does not rely heavily on vendor quotations that may or may not be accurate.

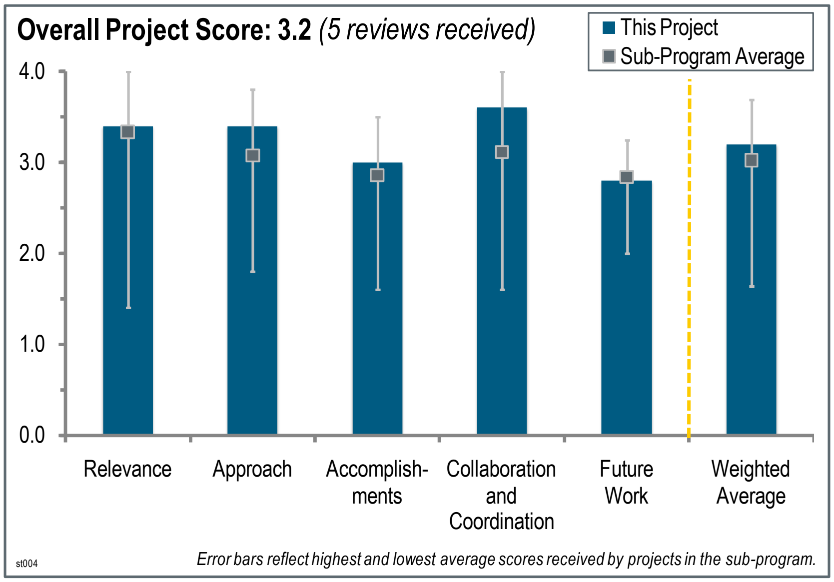
Recommendations for additions/deletions to project scope:

- This reviewer wonders if the BOP can be simplified to reduce costs and if carbon fiber costs can be reduced by looking at different ways of developing tank costs. It is recommend to consider analysis based on textile-grade peroxyacety-nitrate/acrylate fiber.
- It would be useful to state the most imporant factors in establishing the cost of MOFs and other adsorbent materials, such as solvents, to guide the selection of viable adsorbents.
- It is critical to get better cost assumptions on BOP. It is recommended to check into and understand the reasons behind the more basic, low-level approach to the analysis this year to ensure that it is an effective method and philosophy.
- A rudimentary cost analysis for the AB/IL system is needed. Given the fact that the project is nearly complete, it is recognized that the lack of remaining funds would preclude even a cursory analysis at this time.

Project # ST-004: 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 U.S. Department of Energy (DOE) hydrogen storage programs to compile their media and systems requirements and data; (3) identify the current state-of-the-art for metal hydride, chemical hydride, and adsorbent hydrogen storage systems; (4) identify the technical barriers to be overcome in achieving the 2015 Onboard Hydrogen Storage System Technical Targets; (5) identify solutions to overcoming these barriers; (6) demonstrate subscale prototype systems for each of the storage system types; and (7) disseminate the new design tools, methodologies, and component requirements needed to develop condensed-phase hydrogen storage systems for light-duty vehicle applications.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to DOE objectives.

- The project is aimed at bringing all of the materials-based technologies being studied for hydrogen storage to demonstration, and hence is critical to the DOE Hydrogen and Fuel Cells Program.
- The Hydrogen Storage Engineering Center of Excellence (HSECoE) project is a critical component of the overall Program, and fully supports the DOE's research, development, and demonstration objectives for the development of a practical and commercially viable onboard hydrogen storage/delivery system. However, the absence of a well defined and developed material system that meets DOE storage goals is a serious limitation that could diminish the overall impact of the project.
- The HSECoE is working well on exploring system-level issues, but with no materials showing real commercial potential, it is hard to rate the center's relevance as "outstanding."
- The project goals generally address Program goals and objectives adequately.
- If there is a potential for condensed-phase hydrogen storage employing a solid material, the concurrent materials research and system engineering methodology is necessary to best identify the materials, their research and development requirements, and the systems that best enable them. Onboard vehicle storage requirements present significant challenges to condensed-phase hydrogen storage methods, but the materials and systems developed at the HSECoE can advance commercialization of hydrogen fuel cells in earlier market sectors than the automobile, thereby adding commercial leverage to the acceleration of technology improvements needed for light-duty transportation.
- Revised decision metrics are not sufficiently clear; for instance, what constitutes a "reasonable storage media property?"

Question 2: Approach to performing the work

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

- The organization chart of the HSECoE shows that the work is well designed and addresses practically all important issues.
- The HSECoE has a well balanced approach to considering the most relevant issues around storage. Simulation and costing tools complement experimental projects well. The matrix organization is a good fit for the HSECoE.
- The change in the phase one, two, and three metrics improves the opportunity to identify engineering solutions from the material and system perspective by allowing the ability to present, build, and test reasonable solution pathways. If the balance of plant (BOP) web-based catalog on SharePoint is user-friendly, well populated, and easy to access, this could be very helpful in the engineering and analysis of performance for system design candidates. The validation experiments are not generally for each material area (i.e., metal hydride, chemical hydride [CH], and adsorbent), but specific to the particular material chosen as a surrogate for each material area; with the exception of the solid ammonia-borane (AB) system, which was rejected in the down-select for CH materials.
- The combination of modeling and material and component characterization efforts, design evaluations via modeling, and subscale testing is sound. The incorporation of continuously gathering feedback from various system element providers reinforces the usefulness of the approach.
- The management and participants at the HSECoE fully acknowledge that an ideal material system that meets all of the storage goals is not available. To circumvent this problem (at least in part), the HSECoE has adopted an approach that addresses engineering technical barriers that must be overcome within the embodiment of the system and employ the best materials currently available. The overall approach incorporates the understanding of the technical barriers with solutions to develop subscale prototype systems that incorporate specific classes of materials. Given the state of material development, this is a reasonable and compelling strategy. However, this approach, of course, assumes that the same or similar engineering barriers are encountered by all of the candidate materials within a class (e.g., solid hydride, liquid, or physisorption media). That may not always be the case. Also, the approach demands that very close collaboration and communication be fostered and maintained among all participants, a daunting management and coordination challenge.

Question 3: Accomplishments and progress towards overall project and DOE

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

- Good initial results have been obtained on the development of an integrated model framework and design of subscale prototype systems for different classes of materials. Selection of sodium aluminum hydride ($NaAlH_4$), the high-surface-area activated carbon adsorbent, AX-21, and AB liquid as initial trial media is allowing critical issues relevant to each material type to be identified and preliminary subsystems to be developed.
  The “spider charts” are extremely useful for conveying status of the technology in a straightforward and unambiguous manor and for identifying “priority thrusts” for future work. One area of concern is that alane has not been considered for subsystem development. The promising characteristics of alane make it a candidate material that should not be overlooked even at this early stage of the project. The thermodynamics, kinetics, and transport characteristics differ widely between AB and an alane slurry, suggesting that a generic fluid system design would probably not apply equally well to both. Although it is recognized that the evaluation of a large number of systems is probably intractable and therefore should be avoided, the appealing properties of the alane system strongly suggest that it should be an important part of the portfolio for subsystem development.
- The HSECoE is progressing well in meeting goals. The integrated model is a significant accomplishment. The BOP database is a good development. It will need to be maintained and updated if it is to have long-term value.
- According to the principal investigator, the project is 40% ready. The integrated model framework is set up and the storage system and BOP design concepts are formulated and tested for three major systems based on $NaAlH_4$, AX-21 adsorbent, and fluid (slurry) AB.
- The compilation assessment of the state-of-the-art for materials and their implementation technologies is very important, as is the initial modeling and early validation experiments. The adsorbent work has improved from two decades ago when activated carbon was the most studied hydrogen adsorbent material. However, using the volume and weight comparison charts from Argonne National Laboratory in the February 2011 Cryo Workshop,

the current pressurized cryo-adsorbent deficits in weight and volume seem to be in the same situation that pressurized cryo-carbon was in 1993. At that time, the idea of removing the weight and volume of the adsorbent material showed that a cryo-compressed tank without the adsorbent improved the volumetric and gravimetric densities over the adsorbent version. This still seems to be the case, even with new materials. This reviewer asks if this will be an issue in rationalizing continued development of adsorbents for hydrogen storage, or if other performance properties are of high enough priority and benefit that they will keep adsorbent development as a viable alternative. The integrated model framework appears to be well conceived and executed. System cost continues to be a significant hurdle, and it is not clear if targets can be approached.

Question 4: Collaboration and coordination with other institutions

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

- The project has engaged important collaborators from industry and academia who have made important contributions.
- This is a large and complex center with subject matter experts and subtasks comprising distinct, but complementary areas of emphasis and focus. Extensive collaborations exist among partners in the HSECoE and with external organizations. A solid management plan is in place and good communication channels seem to exist. This reviewer feels that the HSECoE's coordinating council should play a vital role in promoting collaboration and coordination, and identifying critical areas for study.
- The basic concept of HSECoE is to put several institutions into close collaboration and provide them with good coordination.
- With a center this large, achieving effective communication with collaborators is difficult. It would have been good to hear more about how the center is managed and what measures are being taken to achieve the right balance of interaction among participants.
- While the efforts presented showed very good collaboration among the stated partners, the HSECoE presentation was not sufficiently explicit in showing the roles of the partners.

Question 5: Proposed future work

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

- The proposed future work is sharply focused on the main barriers that still need to be overcome in the project.
- The technology-thrust areas highlighted in the spider charts provide a straightforward, detailed, and clear description of future work. However, it is strongly recommended that the critical issues underlying the development of a storage/delivery subsystem based on alane be included in the future work.
- It would be helpful to know how much of a potential impact the future work has on the viability of the storage systems. That is, whether the HSECoE projects have the potential to make a system meet or exceed targets, or if the work will just make the systems better but still well below targets. Making models widely available is a good goal for the future.
- The metal hydride and adsorbent future work will address improvements in media compaction and media thermal conductivity by engineering methods. Compaction and thermal conductivity behavior are both related to deficiencies in gravimetric and volumetric densities. The reviewer asks what engineering modeling effort has been conducted in phase one to understand whether the proposed future work will ever bring the technologies close enough to DOE's 2015 targets.
- Technical-thrust areas are identified, but there are no clear plans on how these areas will be addressed.

Project strengths:

- The HSECoE comprises a strong, diverse team with expertise and experience in all principal areas that are vital to the modeling and engineering development of viable storage/delivery subsystems. The approach is well formulated and the results to date suggest that the team is on the proper path to achieving the project goals.
- This project has a strong team and collaborations. The HSECoE's approach is well thought-out and executed.
- This project has a good structure and design with excellent collaborative partners.

- The main attracting feature is the flexibility of the collaborators' reconsideration of the HSECoE go/no-go decision metrics, and the adequate response to the comments of reviewers during last year's Annual Merit Review.

Project weaknesses:

- The primary weakness of the project (not a fault of the HSECoE) is that there is no single material that meets DOE's objectives for hydrogen storage. Consequently, the HSECoE is forced to develop systems for less capable, surrogate materials. Athough the decision to focus on generic engineering barriers for each media category is reasonable, it assumes (sometimes incorrectly) that all materials in a certain class face common challenges.
- The HSECoE's main weakness is the lack of good materials to model and engineer. This is not a fault of the HSECoE.
- There is not enough focus on cost, and the softening of success metrics could lead to useless work toward untenable systems.

Recommendations for additions/deletions to project scope:

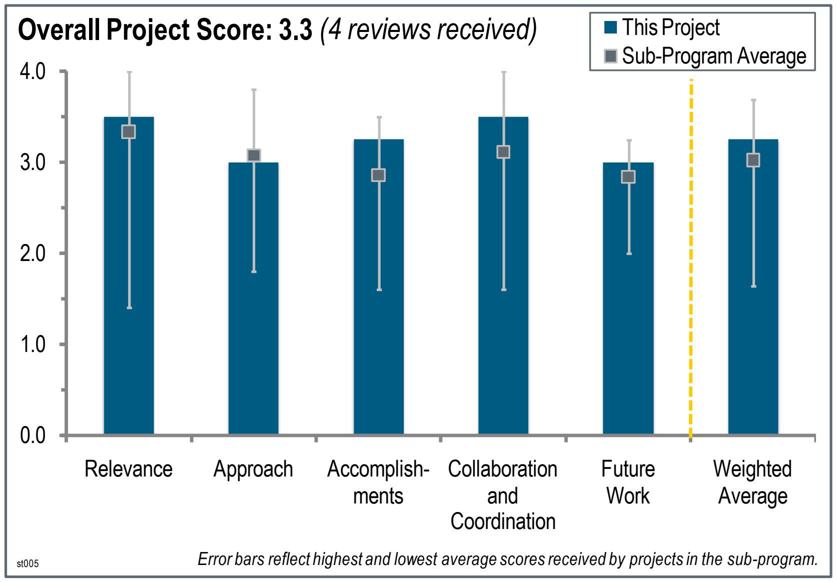
- It is desirable that all of the proclaimed barriers are reached.
- The researchers should include modeling and design of a subsystem based upon an alane slurry as a storage/delivery medium.
- Note to DOE (not the HSECoE): The presentation was an overview of the HSECoE's technical accomplishments, which was good for the general audience and to preview the results of individual projects for reviewers. The Program should consider a separate presentation, perhaps just for reviewers, to evaluate center management and operational issues.

Project # ST-005: Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for Onboard Hydrogen Storage

Jamie Holladay; Pacific Northwest National Laboratory

Brief Summary of Project:

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



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.5** for its relevance to U.S. Department of Energy (DOE) objectives.

- Pacific Northwest National Laboratory (PNNL) supports the activities of the Hydrogen Storage Engineering Center of Excellence (HSECoE) from various points of views, including down-selecting candidates for onboard storage material and the process for the material.
- This project addresses most component-related aspects of hydrogen storage systems for light-duty vehicles. It is focused on demonstrating storage system performance and cost levels that meet or exceed DOE's 2015 targets (slide three). Chemical hydrogen storage materials, selected pressure vessel properties, and general storage system behavior with respect to materials compatibility and component durability are studied. Critical input for "go/no-go" decisions emanate from this project.
- Ultimately, the development of an engineering solution designed to overcome materials deficiencies is expected to enable materials utilization.
- The first stated task in the "relevance" slide is to "demonstrate hydrogen storage system that meets DOE 2015 targets for light duty vehicles using chemical hydrogen storage." Clearly that is an ultimate goal for chemical hydrogen storage materials, but there is not a clearly portrayed schedule, or other descriptor that shows the gaps or reasonable expectations for the approaches chosen. The task to "identify minimal performance for materials to be applicable in engineered hydrogen storage systems for light duty vehicles" is very important for chemical hydrogen storage materials systems and is the primary task that drives all of the other task statements in the "relevance" slide.

Question 2: Approach to performing the work

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

- The approaches, in general, are appropriate.
- The approach is generally what seems needed to accomplish the main objectives (slide five). However, the work scope appears to be a bit scattered in that it addresses only one type of storage material (chemical hydrogen

storage materials), works on enabling technologies for pressure vessels, and does another body of work that is supposedly relevant to all storage systems. There is a wide diversity of tasks.
- This project has a well structured approach. However, it is important to emphasize that an acceptable material properties range based on the sensitivity analysis generated from the system design needs to be provided eventually.
- It is interesting that the reactive transport concepts for dry ammonia-borane (AB) and AB/methyl cellulose were deselected, apparently for the not-surprising failure of an auger reactor. Augers are difficult devices when the powder bridges or changes packing fraction or other flow properties within the auger itself. There are other conveying reactors for dry AB and AB mixes that have shown to be successful for hydrogen production on a multi-kilowatt scale. It is difficult for most people to imagine using something other than a gas, liquid, or slurry to fuel a vehicle, but a solid/gas dispersion or mechanical conveyor of solids could do the same. The building of the BOP catalog should prove to be a valuable tool for quickly understanding system engineering options. One important consideration is the addition of information to the Society of Automotive Engineers, Underwriters Laboratory, or other certification each component has or does not have relevant to its application to vehicles.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The chemical hydrogen storage materials models and model validation experiments are valuable. Baseline mass and volume projections can now be mixed with the status of other metrics and system-engineer modeling to improve more global projections of each material approach's ability to meet DOE targets.
- The liquid AB was down-selected among eight candidates. It was expected to be tough, but has been well done. Other tasks, such as modeling, are also well conducted under appropriate management of the project.
- The BOP library should prove to be a very useful information repository. The configuration analyses are important, and it is good to see size, weight, and cost estimates coming together in complete systems.
- It was difficult to gauge the specific progress made in this program in the past year. This reviewer asks, for example, how the spider chart on slide seven has changed over the past year as a direct result of the findings of this project. A before-and-after version of the chart might help clarify that matter. Also, the on- and off-boarding of a solid material used a surrogate. Therefore, the test did not demonstrate that the storage material can be kept in a stable state during transfer.
- The kinetic model and reactor concept validation for AB are important accomplishments. The reviewer wants to know, however, if an overlap exists with the Los Alamos National Laboratory's (LANL's) work.

Question 4: Collaboration and coordination with other institutions

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

- Collaboration activities are extensive, appropriate, and well documented in the presentation. The project has many tasks, most of which seem to benefit from input provided by collaborators. A slide showing exactly how and where this project fits into the HSECoE should be included in next year's presentation. This reviewer knows such information was given in the HSECoE overview presentation, but it needs to be seen again in the context of the work of this project.
- There is visible collaboration within the center; however, the relation to Argonne National Laboratory's work does not seem to exist.
- This project has complementary partners and complementary project accomplishments.
- There are a lot of collaborators in this project.

Question 5: Proposed future work

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

- The proposed future work with the HSECoE seems to be fine. However, engineering the design of the tank is closely related to codes and standards.

- This project would be more effective and efficient if it focused on the BOP and cost analysis aspects of all of the viable hydrogen storage materials and concepts and left the chemical hydride work to someone else. The chemical hydrogen storage materials connection may be biasing the BOP considerations. Nonetheless, the future plans build on past progress in a sensible way.
- As a next step, sensitivity analysis based on materials properties/system is crucial, i.e., what ranges should one look at when selecting a material system similar to AB (exothermic, solid, etc.).

Project strengths:

- The leadership of the principal investigator is very impressive in terms of down-selecting from eight process candidates of AB reactors. The wide range of activities in PNNL is also very impressive.
- The identification of gaps in materials properties based on realistic system design is an area of strength.

Project weaknesses:

- Experimental and theoretical work has been done previously by Millennium Cell (out of business) on similar systems. Consultation or access to their knowledge is very important to avoid replicating work.
- Heat management for onboard hydrogen release is critical because exhaust heat from a polymer electrolyte membrane fuel cell is 60°C at its highest. However, analyses done under this project has not included heat management or discussion of the heat of hydrogen desorption. Total energy efficiency should also be considered in any analyses.
- The project seeks to address 10 barriers with a little more than $1 million per fiscal year. At that level of funding, it is a concern that some barriers will not get the attention they deserve and require.

Recommendations for additions/deletions to project scope:

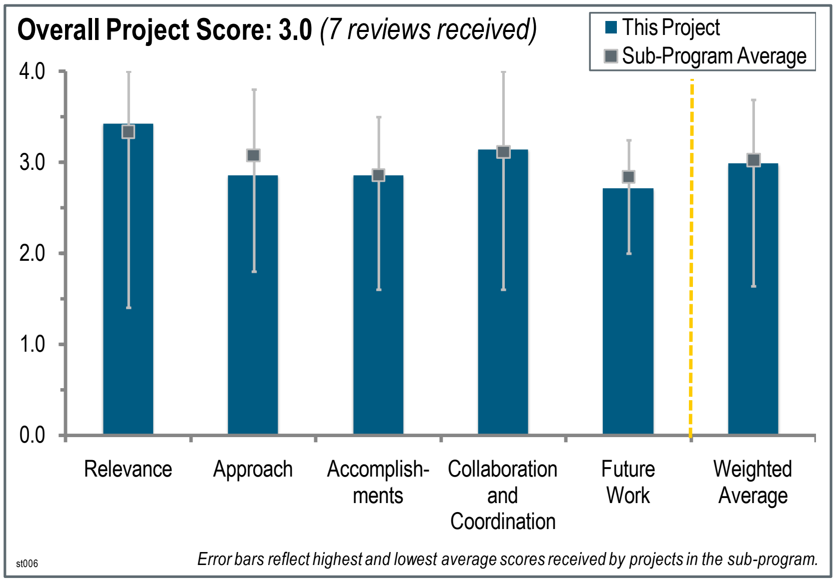
- Consideration of total energy efficiency should be included in any future work. The BOP library is useful if it is updated and opened to original equipment manufacturers (OEMs). The list will be a driver for OEMs to further development and widen their production varieties. Researchers should also start conversing with codes and standards experts.
- In future presentations the comparison basis for spider charts and performance values should be DOE 2015 targets and goals; 2010 targets do not include a 300-mile range vehicle.
- It is recommended that this project clearly distinguishes its scope from LANL's work.

Project # ST-006: Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

Bart van Hassel; 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 hydrogen storage materials, and cryo-sorbents for hydrogen storage. The project approach is to leverage in-house expertise with various engineering disciplines and prior experience in metal hydride system prototyping to advance materials-based hydrogen storage for automotive applications.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to U.S. Department of Energy (DOE) objectives.

- This work relates to the evaluation of several DOE targets with a focus on rates of uptake and release of hydrogen from complex hydrides, along with a study of additives to enhance thermal conductivity. Other work involves the study of absorbent traps for impurities released from hydrogen storage materials.
- The United Technologies Research Center (UTRC) is performing this project as a partner in the Hydrogen Storage Engineering Center of Excellence (HSECoE), and has completed two years of effort. The primary objective of the HSECoE is to address critical engineering issues to accelerate the development of materials-based hydrogen storage systems that can meet all of the DOE targets for fuel-cell-powered passenger vehicles. The specific areas that UTRC supports include developing comprehensive modeling on storage performance, improving the heat exchange properties of material beds via modeling and experimental verification, enhancing volumetric densities of hydride and adsorbent beds via compaction, developing purification components to increase hydrogen purity as delivered to the fuel cell, and assessing safety issues.
- This project is a flagship activity in the quest to demonstrate an onboard hydrogen storage and fuel delivery system that meets DOE targets for a 300-mile range fuel-cell-powered vehicle.
- The relevance of these projects is good. They could be outstanding if materials with commercial promise were available.
- This effort is part of the HSECoE and the development of properties and performances required for a number of materials to enable designs for materials-based storage systems. It is highly relevant to the HSECoE's effort and aligns well with the DOE Hydrogen and Fuel Cells Program's hydrogen storage objectives.
- Effective onboard hydrogen storage is an important enabling element for fuel cell vehicle deployment.

Question 2: Approach to performing the work

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

- The researchers made good use of modeling and experimentation.

- UTRC used its prior experience with fabricating and testing prototype hydride storage beds and general engineering expertise to support the HSECoE goals. A detailed system performance model was developed for comparative analyses of the different storage designs. UTRC also addressed thermal performance properties of compacted materials via theory and laboratory tests on surrogate complex hydrides and carbon adsorbents. Qualitative risk analyses methods were applied to predict potential safety issues for the three classes of storage materials.
- An outstanding approach would be one that addresses every aspect of the hydrogen storage and delivery system for a fuel-cell-powered vehicle. This approach is, in fact, a very well conceived one that addresses most of DOE's targeting aspects that are important at the present time. The reviewer's main concern is that these supposedly cutting-edge projects within the HSECoE still speak in terms of 2010 targets, when in fact the 2015 targets may not get us to a 300-mile range vehicle.
- The approach is built upon previous experience at UTRC with hydrogen storage in metal hydrides. Sodium aluminum hydride ($NaAlH_4$) and lithium (Li)-magnesium (Mg)-nitrogen (N) hydride were chosen for the initial model development. Efforts were focused on determining and enhancing the thermal properties and performance of these materials. Compaction, heat exchanger designs, and a means of enhancing the thermal conductivity of these materials were studied. These studies provided input to the integrated model framework to determine vehicle performance on a common basis among several materials-based storage systems. Other participants concentrated on other materials within their expertise to avoid any duplication of effort.
- The compaction work is a good start. Because materials will be subject to vibration and mechanical stresses, non-static tests should be performed and fines production measured. The project appears to be working on several issues and achieving moderate but insufficient progress. It might be worthwhile to consider focusing on one problem (such as pelletization) with the goal of developing a strategy that would settle whether the material would ever be able to sustain the 1,500 cycle requirement. It was not obvious how the team is carrying out the risk analysis. If not already doing so, it should use industry-standard methods for hazard recognition, analysis, and assessment (e.g., Hazard and Operability Studies).
- The approach elements are described, but there is no indication as to their order or dependency. There are not clear criteria for progression to phase three.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- This project accomplished beautiful results on thermal conductivity measurements in $NaAlH_4$ and initial studies of Li-Mg-N materials. Understanding the different behavior in these two complex hydride materials will help to provide insight into complex hydrides as generic materials. For example, understanding why one material needs more or less engineering to obtain the same thermal conductivity. The reviewer asks if there are linear relationships with thermal conductivity of the starting material, how the engineering affects the expansion and strength of pellets, and how mesh reinforcement impacts the thermal conductivity of the pressed powders. The reviewer also wants to know where the qualitative risk analysis is going. Obvious risk and failure mechanisms were outlined. The reviewer wonders if there were any surprises and who will work on mitigation strategies. It will be difficult to categorize the safety of the storage media. The reviewer asks if there is already enough known about materials to have provided a green, yellow, orange, or red label, and how gasoline would be categorized.
- "Significant" is the right word to describe the progress made in this project over the past year. Very few of the system requirements have been met, but much has been learned about critical issues such as compaction, thermal management, fuel purification, and risk factors.
- Both powder and compacted forms of these hydrides were studied. Good progress was made in determining the optimum amount of compaction needed to maximize capacity. The impact on the capacity of mesh supports to prevent the compacts from turning to dust was determined. The effect of conductivity enhancers to enable a fast fill was also determined and heat exchanger designs for fast fills were studied. These results showed that further improvements in materials properties and vessel design would be needed to meet DOE targets. Most importantly, a model framework was developed that will allow simulation of the storage system in a vehicle context, which will allow for determination of gaps and deficiencies in material properties and performances needed to meet DOE targets. Other noteworthy accomplishments were the study of the cleanup and purification of hydrogen released from the storage materials as well as a qualitative risk assessment for the materials-based storage systems.

- In addition to executing extensive system analyses in support of the phase one/two review, UTRC conducted detailed modeling and experiments on the thermal properties of compacted $NaAlH_4$ and Li-Mg-N-H materials beds, including the incorporation of carbon additives that gave enhanced anisotropic heat transfer within beds in order to improve capabilities. However, limitations of current materials do not allow the critical gravimetric and volumetric targets to be met. UTRC also worked on improving the purity of hydrogen released by amides and boranes that included screened materials to remove ammonia levels, although much more development is still needed. The generic risk factors were obtained for each type of storage system; however, because there are not viable candidates for reversible hydrides and tank configurations remain incomplete, additional in-depth safety analyses will probably not be very helpful.
- This project illustrated compaction by pelletization. Researchers should compare all compaction techniques (old and current) in order to finally propose the most appropriate tank design. There has been no real progress in hydrogen quality improvement. Gaps in material properties need to be addressed early on to avoid several iterations for final tank systems (e.g., Pacific Northwest National Laboratory [PNNL] will work on ammonia-borane, hydride-amide systems)
- Physical strength results are disappointing. Pelletization appears to be a no-go until physical strength can be maintained and volume expansion minimized.
- Various treatments and additives were identified and tested, but there is not a clear indication of their impact on gravimetric and volumetric density metrics, let alone cost. Cyclic testing at 15 cycles seems insufficient to characterize volumetric expansion and strength effects. It is not clear from current results whether even 2010 targets can be achieved.

Question 4: Collaboration and coordination with other institutions

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

- This project has good collaborations with complementary research groups. There was a slight difference in units to measure the strength of complex hydride pellets compared to General Motors' (GM) units for measuring the strength of carbon pellets.
- UTRC has worked extremely well with essentially all of the HSECoE partners and other organizations, leading to advances in predicting and improving performance of all three classes of storage media. The tasks appear to have been well coordinated and of great mutual benefit.
- This work includes good collaboration across the HSECoE.
- The HSECoE's concept fosters collaboration among the many participants that might not otherwise be possible. In addition, active guidance from the automobile original equipment manufacturers (OEMs) tends to keep the effort focused.
- Here one must assume that collaborations are what they should be for an effort such as this one. The presentation did not elaborate on how collaboration and communication is accomplished, particularly with the Savannah River National Laboratory (SRNL). The use of the PNNL balance-of-plant library is mentioned, as are "quantitative insights" from Sandia National Laboratories and SRNL. A clearer perspective about how this project interacts with ST-005 (at PNNL) or ST-044 (at SRNL) would be helpful. Many of the issues being addressed in these three projects have commonalities.
- Collaborators are identified, but it is not clear how they are contributing to the effort.

Question 5: Proposed future work

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

- Slide 20 presents the future plan in what this reviewer believes is the best format for purposes of evaluation. All of the hydrogen storage projects should use this format. It not only says what will be done, it gives a time band over which results can be expected. At the projected funding levels for this project, the team is addressing a well considered set of issues for hydrogen storage systems. This reviewer is not overly confident that 2015 targets for the hydrogen storage/fuel delivery system will all be met by the time this project comes to an end, but much will be learned about how such systems can be expected to operate and about the actual feasibility of ever meeting the targets.

- Sensitivity analysis should be emphasized to enable a criteria for materials selection based on the engineering analysis. The work conducted by GM needs to be considered in the system evaluation.
- The future work was described in a Gantt chart as a series of activities. Work should be described in terms of measureable objectives that can be related to Program targets.
- Descriptions of future activities at UTRC are somewhat vague (i.e., slide 20), especially with respect to improving materials properties and the direction of performance analyses. A good path forward was indicated for getter/purification development, especially for removing ammonia.
- Discussion of future work was very brief in the presentation and did not address the path forward to achieve the metrics needed for the next go/no-go decision. Milestones for future work were not addressed.
- Tasks are identified but dependencies are not clear, nor are there any criteria described for the decision points.

Project strengths:

- UTRC has brought very capable technical personnel into the HSECoE team. UTRC provided sound theoretical modeling, materials characterization, designing, and fabrication of useful prototype components (i.e., compacted bed with improved thermal conductance via the carbon additives). UTRC has the capability to contribute to improving properties of very diverse materials and operating conditions. A good balance was made between modeling and experimental assessments.
- This project has a knowledgeable, experienced team and the right combination of modeling and testing tools. This project's presentation was done very well.
- The approach and facilities are this project's strengths.
- This project has excellent collaboration among the team members and there has been good progress since the last Annual Merit Review. The data and information obtained should be indicative of the deficiencies in materials properties and designs that need to be addressed to prove the feasibility of a storage system that meets DOE targets.

Project weaknesses:

- There are very few issues with the quality and innovation provided by the UTRC technical staff. However, the chemical and physical limitations of each of the current candidate materials create major hurdles for researchers to overcome if DOE performance targets are to be reached using the approaches currently being developed.
- There are more difficult problems and issues to resolve than the allocated funding is likely to allow.
- There is no clear definition of the criteria for success for pelletization. It is unclear if unspecified property improvement is enough, or if success should be tied to Program goals.
- The complex management structure could lead to the fragmentation of efforts and a loss of focus, particularly in the modeling area. Continued guidance from the OEM partners as well as from DOE will be required.
- It is not clear from current results whether even 2010 targets can be achieved.

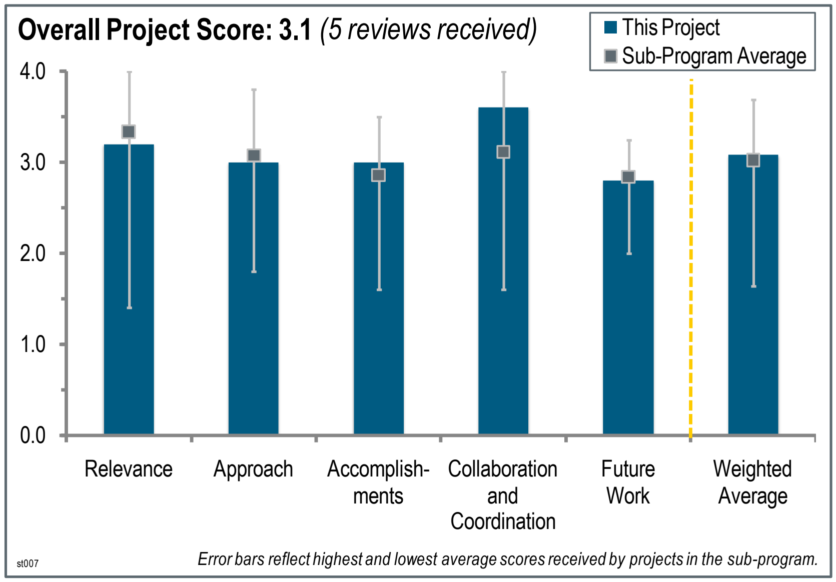
Recommendations for additions/deletions to project scope:

- UTRC should address methods of improving the thermal performance of generic storage materials rather than conduct trade studies on requirements that a storage material should have. Optimizing heat and mass transfers while reducing mass and volume of the storage vessels would be very valuable to the HSECoE and DOE goals. Further efforts to devise and demonstrate more efficient and regenerable hydrogen purifiers are strongly recommended. Finally, any further risk analysis activities should be curtailed, as it is unlikely that the currently identified materials will be used extensively and system configurations are a long way from being defined. Without more complete specifications of designs, materials, and operating conditions, such risk analyses would not be very reliable or useful.
- The prototype construction and testing task should be reassesed. This should not be undertaken until a material is in hand that can meet the DOE targets in a system with a realistic chance of being viable. It may be necessary to limit consideration to only one system to achieve a successful outcome. The schedule for down-selection should be reassessed to reflect current and reasonably expected progress.
- Reversibilty needs to be illustrated through cycling to determine the best way of compacting materials.
- This project should use industry-standard hazardous operation analysis.
- The researchers should forget 2010 targets and move onto exploring what can be done to meet and even exceed 2015 targets.

Project # ST-007: Chemical Hydrogen Storage Materials 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 (HSECoE), 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 hydrogen storage materials. 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 hydrogen storage materials; (4) develop novel reactor designs for start-up and transient operation with chemical hydrogen storage materials; (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 hydrogen storage materials.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.2** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project is a vital component of the HSECoE and the technical effort in this project fully supports DOE's Hydrogen and Fuel Cells Program and research, development, and demonstration objectives. As a technology lead for chemical hydrogen storage systems, the project addresses some of the most important (and challenging) technical issues encountered in the HSECoE.
- There are many diverse elements in this project. If chemical hydrogen storage materials or metal hydrides move forward for transportation, most of the goals of this project will be relevant to the Program. In addition, the possibility of not meeting the goals for transportation applications does not invalidate the efforts. There are many other applications where the chemical hydrogen storage materials work can prove to be commercialized earlier than the fuel cell automobile. This can, in turn, accelerate the commercialization of automotive fuel cell systems by improving related technologies in the marketplace more quickly than it can happen for transportation alone.
- Effective onboard hydrogen storage is an important enabling element of fuel cell vehicle deployment.
- LANL is conducting this project as a partner in the HSECoE and has completed two years of effort. The primary objective of the LANL work is to address critical materials and engineering issues in the development of chemical hydrogen storage systems that can meet all of DOE's targets for fuel-cell-powered passenger vehicles. The specific roles that LANL covers include serving as the system architect and lead designer for fluid-phase chemical hydrogen storage systems, developing models for hydrogen release and degradation of chemical storage materials, designing and testing subscale reactors, developing purification components to increase hydrogen purity as delivered to the fuel cell, and developing fuel gauge sensors for hydride vessels.

Question 2: Approach to performing the work

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

- Building upon its expertise as a co-leader of the HSECoE, LANL has led the work to develop ammonia borane (AB) storage systems. After extensive assessments and reviews, liquid-based solutions and slurry work is moving forward. LANL actively participated via internal modeling and contributing to analyses by other HSECoE partners. Researchers paid good attention to developing systems that could meet DOE targets.
- For a project of this complexity and breadth, it looks well planned out. The surrogate selection of AB as the fluid chemical hydrogen storage material system fuel defines the reactor system, process, and balance of plant (BOP). If AB is eliminated in the selection, the systems developed may still be able to be used for other chemical hydrogen storage material system candidates with some modification. The principal investigator mentioned that the cost of AB and/or the regeneration process is projected to be $9 per kilogram. (This reviewer is not sure whether the cost referred to in the presentation was for AB or the AB regeneration cost.) In either case, this seems very optimistic. It is important, in a DOE-funded project, to have a rationale that has some basis in the projected cost of a currently costly commodity or process. The basis for that cost then needs to be clearly shown. There needs to be an effort to establish a method of numerically prioritizing each barrier depending on the application so that 1) the value of the project is not diminished by disproportionately downgrading it based on specific barriers, or 2) we do not miss the ability to make engineering trade-offs that permit a system to be useful even though there is a stand-out barrier that is not perfectly addressed. The iconic examples are those of volumetric and gravimetric densities. This would be a good project for such an engineering trade-off approach.
- Each of the tasks that make-up the project appear to be reasonably well conceived, though more detail could have been provided for a number of the tasks.
- In 2010 and 2011, the project focused specifically on modeling and designing novel chemical storage and delivery subsystems; developing accurate, non-intrusive fuel level monitoring; and identifying and reducing hydrogen impurities. The approach comprises subtasks devoted to system modeling, demonstration, validation, and hardware fabrication and testing. The approach is well formulated and focused on overcoming the important technical barriers. There is a close connection with a recently completed chemical hydrogen storage materials research and development project at LANL. The transfer of understanding and technology from that project, especially with regard to properties of AB/Ionic Liquid systems, is a significant benefit.
- Automotive scale system design does not seem appropriate at this time given that the reactor and system designs are being developed and validated.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- Good progress has been made on the development of a preliminary system design and validation test bed for a liquid-phase subsystem and on the development of a non-invasive fuel gauge sensor. It would have been useful for presenters to include more detail concerning the criteria and approach used in selecting the fluid-phase AB system (LANL) over the solid-phase AB system investigated at Pacific Northwest National Laboratory (PNNL). Both approaches have advantages and disadvantages. The selection methodology should have been described more thoroughly. Given the fact that a fluid-phase approach was down-selected, it would have been useful to examine the trade-offs that must be considered for implementing different kinds of fluid-phase media; currently the two leading candidates are AB and alane slurry. Because these media have different chemical and physical properties, it seems likely that different system design criteria must be invoked. Excellent results were obtained on the acoustic fuel gauge sensor. Proof of concept has been demonstrated and a solid plan for extending the work to liquid systems is in place. The hydrogen impurity work is also important and the LANL team has responded in a timely way to previous review suggestions to focus more closely on this topic.
- LANL has designed and analyzed a solution-based AB storage system that meets or nearly meets DOE's 2015 storage targets; however, several key components still need experimental validation. LANL also continued to identify reaction conditions and compositions that could reduce the formation of ammonia and highly detrimental boron impurities. Further progress and more understanding of decomposition processes are needed.
- The acoustic fuel gauge is a key output, as it could be used for any materials-tank system.

- While a system design has been completed, it incorporates admittedly unproven aspects in the reactor, separation, and purification elements. The test bed should help resolve the suitability of these design elements.

Question 4: Collaboration and coordination with other institutions

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

- LANL has worked extremely well with various HSECoE partners and other organizations, leading to advances in predicting, down-selecting, and improving the performance of chemical hydrogen storage media. The tasks appear to have been well coordinated and of great mutual benefit.
- Close collaboration with HSECoE partners is evident, and those interactions are clearly playing an important role in defining the technical direction taken in this project. Interactions with Brookhaven National Laboratory on characteristics and properties of alane slurries are encouraged if recommendations to pursue that system are adopted. The project is well managed and there is good interaction with the HSECoE technical management and coordinating council.
- The presentation conveyed a good job of coordination among the many partners.
- Collaboration on BOP is visible.
- Collaborative partners were identified, but more details regarding their contributions should have been provided.

Question 5: Proposed future work

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

- This project's future plans are clearly stated and should extend the current work in a straightforward and productive way. It is recommended that the LANL team include a consideration of alane slurries as storage media in its plans for a fluid-based storage/delivery subsystem.
- This project's future efforts are reasonably defined by tasks relative to deliverables, milestones, and decision points.
- LANL's plan to perform validation testing of conceptual reactor designs and several other important components, such as gas/liquid phase separators and hydrogen purifiers, for the liquid-based AB media is excellent and should be fully supported. However, more attention should be focused on understanding the formation of harmful boron impurities during storage and decomposition reactions. There did not seem to be any plans for considering other kinds of chemical hydrides, such as alane slurries.
- It is recommended that the roles in United Technologies Research Center's (UTRC) impurities mitigation work and PNNL's work on kinetics modeling and validation of prototypes are determined to avoid overlap.
- In terms of future work for the fuel gauge, this reviewer wants to know how physical change of the metal hydride, such as decrepitation, affects the gauge performance. In the cycling-of-charge in a gauge test, the team should check the long-life-cycle ability of the hydride and its effect on the measurement.

Project strengths:

- LANL has brought very capable technical personnel into the HSECoE team that provided sound theoretical modeling and materials characterization of chemical hydrogen storage materials, especially AB. A good balance was made between modeling and experimental assessments. A very comprehensive assessment of alternative design for both solid and liquid AB reactors in support of the phase one/two transition review was conducted. The knowledge and experience from the former Chemical Storage Center of Excellence was an excellent benefit in all of the HSECoE tasks.
- The project team has extensive background and expertise in fluid-based systems and acoustic sensors. There are robust and valuable collaborations with other HSECoE partners.
- This is a multifaceted project that is adequately structured and making acceptable progress.
- These technologies (e.g., sensors, BOP database) could be applied to different tank systems and be utilized by other members.

Project weaknesses:

- There are no issues with the breadth of effort and innovations in the design of several components for chemical hydrogen storage systems. However, nearly all of this effort has been on AB, with virtually no attention being given so far to other exothermic or endothermic (e.g., alane) hydrogen absorbers. The amount of resources devoted to the feasibility of an acoustic fuel-gauge sensor was a distraction to the primary focus of this project. While this device is certainly innovative and may someday be applicable to hydride beds, this reviewer believes LANL should have done this work in a different project instead of the HSECoE tasks.
- There seems to be an overlap between LANL and PNNL's work on kinetics modeling, validation, and prototyping. For example, PNNL's work on solid AB and proposal to study slurry liquid systems is very related to the liquid-AB work at LANL. Another example is the unclear relation on impurities mitigation between UTRC's and LANL's scopes. It is strongly suggested that roles are distinguished to clarify the collaborations and avoid overlap and duplications.
- A candid acknowledgment and statement of technical obstacles and challenges as well as risk mitigation strategies are needed. Without that information, it is difficult to assess and prioritize the most urgent problem areas that should be addressed in future work. For example, there are thermal stability and impurity issues that may deleteriously affect the properties of ionic liquids. Mitigation strategies should be part of the overall plan.
- There was little discussion of system cost.

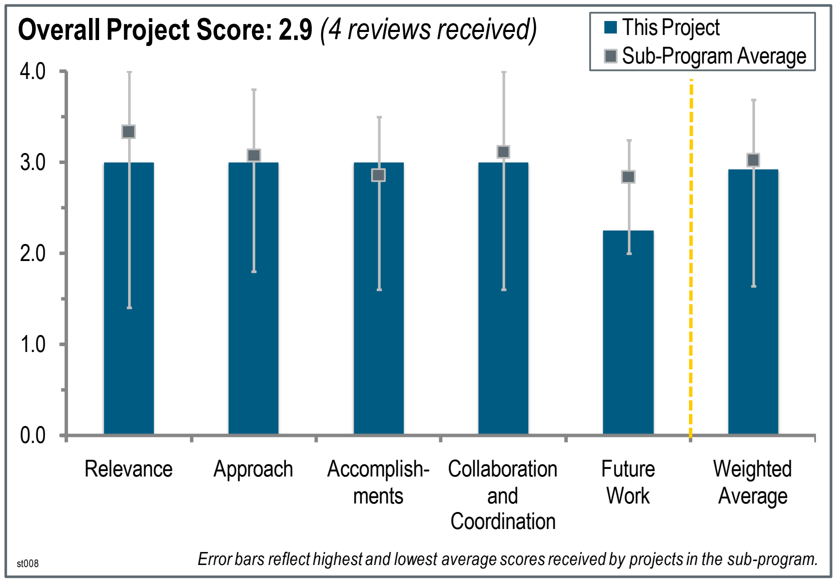
Recommendations for additions/deletions to project scope:

- LANL should proceed with the verification testing activities described in its presentation rather than conduct more detailed modeling or trade studies on theoretical configurations of AB containers. Continuing efforts should be made to devise and demonstrate more efficient and regenerable hydrogen purifiers with an emphasis on the diborane and borazine species. However, it would be best to develop AB materials that do not form these impurities during aging or hydrogen release. This reviewer strongly recommends that any more work on the acoustic fuel sensors is discountinued within the scope of HSECoE efforts.
- There should be more of a focus on fuel gauges, in the opinion of this reviewer. LANL's scope should be distiguished from UTRC's and PNNL's scope. Work on the automotive bench scale should be postponed until reactors systems are confirmed.
- The LANL team is strongly encouraged to include a consideration of alane slurries in its proposed design for a fluid-based system. Although the alane system is a top contender for continued development, the chemical and physical properties of that system are significantly different from AB. Consequently a "generic," fluid-based system using AB may not directly translate to a system using alane.

Project # ST-008: 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 project is to provide system design, analysis, modeling, and media engineering properties for hydrogen energy storage. Objectives for the project are to: (1) coordinate the Hydrogen Storage Engineering Center of Excellence (HSECoE) performance, cost, and energy analysis technology areas; (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 center in the identification and characterization of sorbent materials that have the potential for meeting U.S. Department of Energy (DOE) technical targets as an onboard system.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.0** for its relevance to DOE objectives.

- The National Renewable Energy Laboratory (NREL) is performing this project as a partner in the HSECoE and has completed two years of effort. The primary objective of the NREL work is to provide vehicle system performance information and constraints that impact the development of three materials-based hydrogen storage systems and to help identify ways of meeting the DOE targets for fuel-cell-powered passenger vehicles. These results were pertinent for establishing the boundaries used during the phase one/two review. However, in the absence of truly viable near-term configurations that can reach these targets, there is little need for further refinements of these models. NREL also provided updated information on alternative adsorbents that could be assessed further if HSECoE had more resources.
- This tool allows center participants to evaluate the effect of storage systems on overall vehicle performance, a valuable addition to center researchers.
- This part of the HSECoE coordinates the modeling activities taking place in the center. Coordination is necessary to prevent duplication of effort within the center and to leverage modeling activities outside of the center. This activity supports the DOE Hydrogen and Fuel Cells Program objectives.

Question 2: Approach to performing the work

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

- The approach is generally good, but coordination of modeling efforts is needed. If the HSECoE is mainly charged with developing materials properties and validated storage system designs, modeling should be focused on this objective. WTW and GHG impacts can best be accomplished in other parts of the Program. Similar comments can apply to the cost. Unless the original equipment manufacturers (OEMs) are planning to cost the

final design concepts, cost analyses should be left to TIAX and Directed Technologies, Inc. (now part of Strategic Analysis, Inc.). The presentation did not indicate the relative level of effort among the modeling tasks.
- The development of vehicle and storage systems simulations by NREL has given an overview of requirements imposed on the storage configurations that are necessary to reach DOE performance targets, which helped to focus the go/no-go assessments during phase one. However, it is unlikely that extended analyses can directly lead to the materials discoveries and engineering improvements that HSECoE will need to examine during phases two and three.
- WTW energy analysis and cost trade-off models at the vehicle system level are important for technology feasibility.
- Integrating storage system performance with vehicle models seamlessly provides ease-of-use to storage researchers. Simple links to models providing WTW analysis would be a good addition.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- It appears that reasonable progress has been made. It would be helpful if the presenter clearly pointed out what was new for this year. It would have been nice to hear more about modeling results. For example, it is unclear if there were any systems that were unable to meet drive-cycle demands. The reviewer also wants to know if there were systems that performed poorly at near-empty tank conditions.
- The vehicle evaluations conducted by NREL during phase one were useful contributions. They provided a common framework for relating the performance levels and limitations of the three materials options. It is unlikely that much more benefit will come from more of these studies. Detailed engineering designs and testing are now needed from the HSECoE partners.
- The major accomplishment appears to be the creation of the hydrogen storage simulator that can be used to evaluate candidate storage systems with a consistent set of assumptions. The simulator was used to model the performance of a sodium aluminum hydride ($NaAlH_4$) system in a mid-size sedan. Numerous drive cycles were analyzed. In order to fully stress the storage system, multiple cycles in the simulator need to be run until the storage system is empty.
- WTW is based on a Hydrogen Storage SIMulator (HSSIM) model for $NaAlH_4$.

Question 4: Collaboration and coordination with other institutions

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

- NREL actively collaborated with several of its HSECoE partners as well as other organizations in developing the simulation models and providing outputs during the phase one tasks.
- There is good work among the researchers across the HSECoE.
- Collaboration within the center is very good. OEM participation can help to keep the focus where it should be, on a validated hydrogen storage system model.
- There is collaboration among HSECoE participants in order to obtain parameters for the model. The project is relevant to Argonne National Laboratory's (ANL) work; however, collaboration between the center and ANL is not visible.

Question 5: Proposed future work

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

- NREL intends to extend its vehicle system analyses to a few storage candidates as summarized on slide 32. However, it is hard to see how innovations in the critical issues necessary to improve performance of these storage concepts will benefit from the proposed extended vehicle system analyses.
- The proposal for polyether ether ketone (PEEK) media and platinum and activated carbon—isoreticular metal-organic framework (Pt/AC-IRMOF-8)—utilization seems to be beyond the scope of the down-selected materials. The model needs to be flexible to allow different material systems.

- The modeling activity will continue to run storage system simulations to evaluate materials of interest. This should be the focus of the modeling effort. Effort to evaluate WTW, GHG, and hydrogen costs should be minimized. That work is best left to other parts of the Program.

Project strengths:

- NREL has a strong modeling capability concerning vehicles and fuel-cell-powered systems that assists in comparing the potential of other subsystems such as hydrogen storage vessels. As the former lead organization of the Hydrogen Sorption Center of Excellence, it remains an excellent information source on the properties and potential of adsorbent materials.
- HSSIM model creation is a strength.
- There is demonstrated modeling expertise in this area.

Project weaknesses:

- The analyses by NREL, while useful for comparing vehicle performance, give little insight into the approaches that can be implemented in material development or engineering improvements.
- From the presentation, it is unclear what the accomplishments were since the last Annual Merit Review. It is not clear how the coordination of modeling efforts occurs, or what the role is of the coordinator.

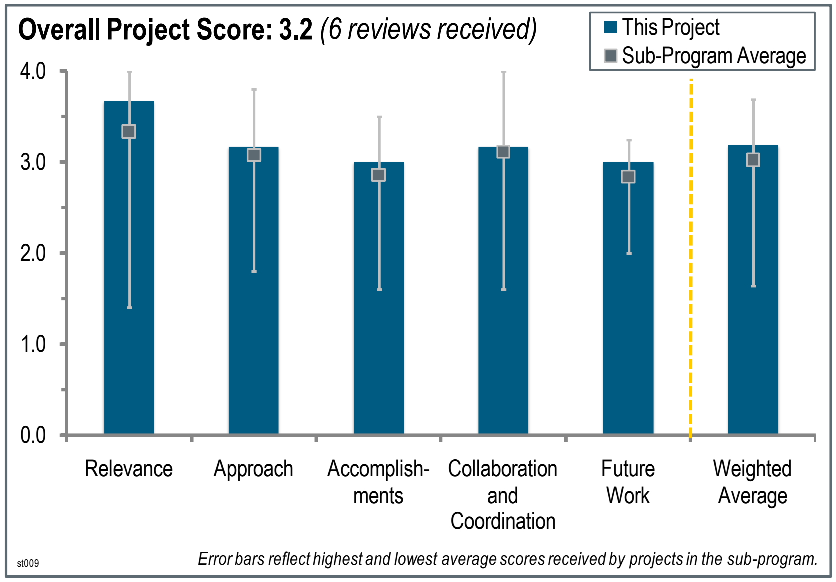
Recommendations for additions/deletions to project scope:

- Although NREL made valuable contributions to the HSECoE during the phase-one tasks up through the go/no-go decision, it cannot provide the detailed technical inputs needed to develop improved designs for hydrogen storage systems. Hence, NREL should complete its direct support at the end of fiscal year 2011 so that DOE resources can be directed elsewhere.
- PEEK media and Pt/AC-IRMOF8 utilization seems to be beyond scope; it is strongly suggested that researchers focus on one system and use sensitivity and trade analysis to help judge other similar material systems.
- NREL should consider making the modeling tool available to persons outside of the center. Web-based access would be a major addition.
- The scope of the modeling activity should be narrowed to evaluating the performance of onboard hydrogen storage systems.

Project # ST-009: Optimization of Heat Exchangers and System Simulation of Onboard Storage Systems Designs

Darsh Kumar; General Motors

Brief Summary of Project:



The overall objective of this project is to develop systems for onboard storage of hydrogen for motor vehicles. Objectives for the project are to: (1) develop system simulation models and detailed transport models for metal hydrides using detailed two-dimensional models of heat transfer, chemical reactions, guide system models, and novel and optimized heat exchanger designs; (2) build system simulation models and detailed transport models for adsorbent material hydrogen storage systems, including activated carbon and metal-organic framework number five (MOF-5) using two-dimensional models of adsorption and heat transfer, and identify system operating conditions for high-gravimetric density; (3) test metal hydride and adsorbent system simulation models for system performance and performance metrics in relation to U.S. Department of Energy (DOE) targets; (4) explore pelletization of the high-surface-area activated carbon adsorbent AX-21 and sodium aluminum hydride ($NaAlH_4$); and (5) work with other Hydrogen Storage Engineering Center of Excellence (HSECoE) partners for integration of hydrogen storage models in a common framework with vehicle system models and fuel cell models.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.7** for its relevance to DOE objectives.

- Optimization of heat exchangers and system simulation of onboard storage system designs is significantly important. The reviewer personally believes that the materials should be down-selected from the engineering to reality.
- The project is critical to the DOE Hydrogen and Fuel Cells Program.
- The design and optimization of heat exchangers and system simulation of onboard storage systems is one of the critical tasks of the Program, and the project supports DOE objectives.
- This project focuses on the development of storage system models and design of heat exchangers for metal hydride and cryo-adsorption storage systems. Efficient heat transport and removal are key issues in the design and development of storage/delivery systems. The work on this project is relevant to the overall DOE research, development, and demonstration objectives, and it supports the technical effort of the HSECoE.
- This work can be very helpful in understanding the heat exchanger designs, pelletization effects of $NaAlH_4$, and Brunauer-Emmett-Teller surface area as a function of compaction of adsorbents and adsorption in hydrogen storage applications.

Question 2: Approach to performing the work

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

- The approach for the tank design and compaction of materials looks conservative. The reviewer expected a little bit more challenge in tank design and taking various options for making the materials more compact.

- The source of the experimental data used was requested.
- System design was based on $NaAlH_4$. Addressing the problems related to other systems would be helpful. Helical coil design approach is good and may offer low heat exchanger weight with lower cost than the dual-bed system.
- The project is well designed and is also integrated with efforts of other parties.
- The approach is logical and addresses the major issues related to efficient heat transport in hydrogen storage/delivery subsystems. The selection of $NaAlH_4$ as a surrogate metal hydride material should allow results needed by the system developers to be obtained in a timely way. Also, in collaboration with Savannah River National Laboratory (SRNL), a solid approach and methodology are in place for the design and development of efficient cryo-adsorption systems.
- The project has a nice approach with a coordinated mix of modeling and experiment. Modeling of the three heat exchangers for metal hydride shows benefits for helical coil over the shell and tube design. The reviewer is unsure about the claim in the principal investigator's presentation that turbulence in the helical results in 2.5 times more heat transfer from the increased turbulence in the helical tube, versus the straight tube.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The team worked hard and the achievement is not so surprising. The reviewer would like to see steady progress in the research and development.
- Progress related to system weight and volume, including energy efficiency, are lacking.
- The project has run for about one-third of the planned project duration and considerable progress has already been achieved. "Surrogate" $NaAlH_4$ systems, the dual bed system, and three heat exchanger designed systems were optimized and considered in detail. The cycling, capacity, thermal conductivity, and pellet expansion of $NaAlH_4$ and pelletized AX-21were studied.
- Good progress has been made on design and modeling of heat exchanger subsystems for metal hydrides ($NaAlH_4$ serves as a surrogate material). In the presentation of the helical coil design, it would be useful to quantitatively show the trade-off or functional relationship between material capacity, sorption enthalpy, and number of vessels that are needed. There was a prior study in collaboration with Sandia National Laboratories and Lawrence Livermore National Laboratory on a testing and validation sodium alanate test bed. It is not clear to what extent the present project has been able to build upon the results of those studies. The modeling of cryo-adsorption systems is more preliminary than the metal hydride work, but good initial progress on system design considerations has been made.
- The heat exchanger models were nicely done. The reviewer would like to see other geometries in the future. The cycling expansion of $NaAlH_4$ pellets is useful data. The AX-21 data for the effects of compaction on gravimetric and volumetric densities indicates that compaction masks surface and closes pores, but not proportionally to volume compaction of powder. The experimental data will be very helpful in developing a generic model for pelletizing or compacting adsorbents. Kinetics and transport should also be in the model.

Question 4: Collaboration and coordination with other institutions

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

- This project represents good collaboration with other institutions.
- Collaboration is performed on the base of regular contracts with collaborators on different project goals.
- Good collaborations with other HSECoE partners are evident, especially with SRNL on cryo-adsorption systems and with United Technologies Research Center, Ford, and the National Renewable Energy Laboratory on integrated framework development and incorporation of transport models into that framework.

Question 5: Proposed future work

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

- This year, $NaAlH_4$ was selected as a surrogate material because of the significant amount of data available. However, the future plan shown relies very much on the material(s) the HSECoE selects. If it takes time to design a real tank onboard for the materials selected, it is unclear what will happen next year.
- There are plans to build on past progress, but the researchers need better focus on overcoming barriers.
- The future work is logically planned according to obtained results.
- Future work is closely linked with materials development and selection. Close collaboration with HSECoE partners is required. Incorporation of heat exchanger concepts into the integrated framework adopted by the center is underway. Focus on cost issues and material trade-off analyses should be included in future plans.
- The small experimental test vessel for cryo-adsorbents is a good approach for validating models for convection and other transport. Using confinement to control expansion and thermal conductivity can be valuable, but may be problematic, based on the same efforts done in some chemical hydrides. If it works and is simple, that would be very good.

Project strengths:

- The project is very realistic and treats everything reasonably. People working on this project know the science and technologies of hydrogen storage materials in detail. Only in this project, ΔH, enthalpy change in hydride formation, or heat of hydride formation is seriously discussed.
- Development of an integrated framework including the vehicle, fuel cell, and hydrogen storage system models are important. The group has good publication record.
- The knowledge and expertise of the project team is a solid basis for successful implementation of the project. The team clearly responded to previous reviewer comments.
- The principal investigator has extensive background and expertise in modeling and designing automotive subsystems. There are valuable collaborations with other partners in the HSECoE. The involvement of an automotive partner in the HSECoE provides a good “reality check” for the center.

Project weaknesses:

- The designs of heat exchangers are old fashioned. Conventional shell and tube types and helical tube type have been investigated since the 1970s.
- The project is not fully focused to address the barriers, including the greater flexibility for system models and heat exchanger designs for different materials. The cost of one system design compared to another is lacking because the primary HSECoE partner, Pacific Northwest National Laboratory, did not help.
- There is a lack of evidence that the chosen storage material will be the same type as the “surrogate” materials selected in the project.
- A clear and forthright description of outstanding issues, technical obstacles, and engineering challenges is needed in order to place the importance of the future work in the proper context and to prioritize the subtasks going forward. Likewise, a clear statement of risk mitigation strategies and a more definitive cost analysis are needed.

Recommendations for additions/deletions to project scope:

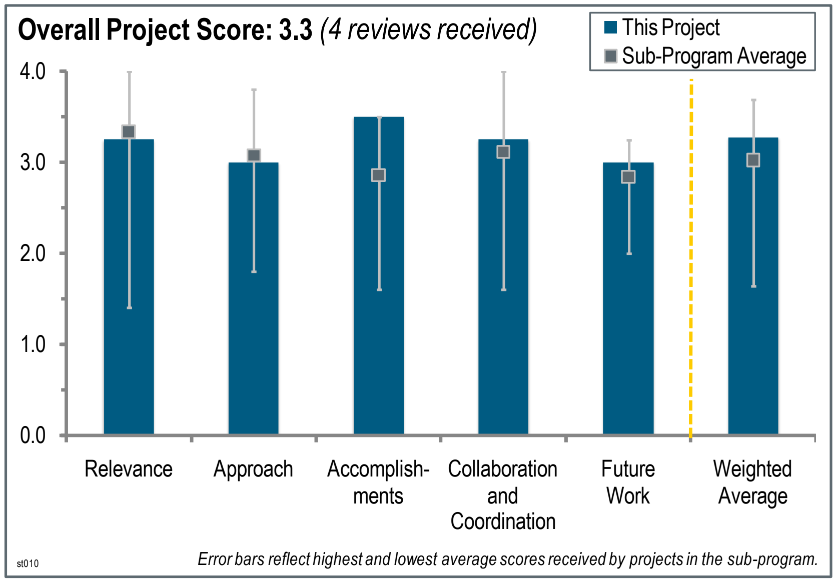
- This year, $NaAlH_4$ was selected as a surrogate material because there was a significant amount of data available. However, the future plan shown relies very much on the material(s) the HSECoE selects.
- A go/no-go discussion on specific heat exchanger designs is recommended.
- There needs to be an attempt to define concretely the future storage material type to consider during heat exchanger design.
- It is recommended that an initial (preliminary) cost assessment be included for all technologies being evaluated and down-selected in the project.

Project # ST-010: Ford/BASF/University of Michigan 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 the 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 framework-based hydrogen storage media.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.3** for its relevance to U.S. Department of Energy (DOE) objectives.

- The project has strong relevance to DOE Hydrogen and Fuel Cells Program goals.
- The project is mostly aligned with the Program goals and objectives. The reviewer believes the types of analyses and investigations that are being performed are exactly what is currently needed. The issues addressed are the right ones and are being addressed with the right mindset. The only exception concerns the choice of sorbent type systems in general and of metal-organic framework number five (MOF-5) and the high-surface-area activated carbon adsorbent, AX-21in particular. As slide 12 showed, the materials capacities of MOF-5 and AX-21 are barely able to match the DOE 2015 system target values, and this is without adding thermal conductivity enhancers or taking full account of the parasitic losses due to having to maintain cryogenic temperatures. Systems studies are showing that the scaling factor from material volume and weight to total system volume and weight is at least 2.0. If the research team cannot make a case that shows MOF-type materials and AX-21-type materials are capable of 11 weight percent and 80 grams per liter (in the fully developed state), the reviewer questions why the team would study them in the first place.
- MOFs have promise to the Program if issues around thermal management can be resolved.
- Effective onboard hydrogen storage is an important enabling element for fuel cell vehicle deployment.

Question 2: Approach to performing the work

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

- The project has a good combination of modeling and experiment.
- The overall approach to all aspects of the work involved in the three tasks addressed by this project is very good. As previously noted, the reviewer is concerned about the materials choices (MOF-5 and AX-21).
- The project has a good systematic approach to compaction and thermal conductivity, and good measurement of pellet stability and properties. The model is an outstanding contribution to the Program.
- The approach is well thought-out in terms of material property assessment and material processing, as well as the resulting uptake characteristics and decision point before prototyping. Modeling and cost efforts are properly designed.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- There are three well defined tasks that contribute to DOE objectives: (1) compactization for sorbent materials; (2) vehicle parameter modeling of drive cycles; and (3) manufacturing costs. Manufacturing costs are not covered in much depth in this review. The reviewer asks if manufacturing costs are now a minor task in the second phase of the project.
- The quality and quantity of the work being done by Ford and its partners at the stated budget level is outstanding. The reviewer believes valuable guidance for making informed go/no-go decisions will emanate from this project.
- This project has shown good results in improving MOF volumetric capacity. Prioritization of system targets is a valuable contribution to the Program.
- Capacity results are good and indicate that gravimetric and volumetric targets could be met in a system.

Question 4: Collaboration and coordination with other institutions

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

- The project has good collaborations with complementary research groups.
- Slides 4 and 26 of the presentation reflect a cohesive connection with appropriate collaborators, most especially the Hydrogen Storage Engineering Center of Excellence (HSECoE). The principal investigator has a key role on the HSECoE's Coordinating Council.
- The project has good collaboration with the center and outside resources.
- The collaborators are clearly identified, well qualified, and making material contributions.

Question 5: Proposed future work

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

- Finding balance to optimize compacting sorbents is important. The reviewer asks if this will change much for different materials, and if so, why that would be the case. The reviewer also asks if this is predictive, meaning that each material need not be measured in great detail. More information on increasing thermal conductivity would be helpful for the next review.
- The plan for the future extends logically from what is currently going on within the project. The reviewer suggests that Ford take an in-depth, hide-nothing look at sorbent materials in general and be prepared to make a case for why work on that type of storage approach should continue.
- Compaction work is largely complete, and plans for thermal conductivity look good.
- The future work is well designed to address technical issues. It is not clear when prototyping will occur.

Project strengths:

- Strengths include a knowledgeable, experienced team; excellent facilities; and expertise of the kind required for this project. The presentation at the Annual Merit Review was very well done. The reviewer found slides 21 and 22 to be very useful and informative. A few of the other slides had too much information and were hard to read.
- The project is making good progress and has unique elements (such as the Target Clasification effort).

Project weaknesses:

- While not a major issue, the reviewer thought slide 15 depicted a really nice experiment that deserved to be described in detail. Unfortunately, it seemed that no one at the presentation could provide that description. Good experimental results deserve to be clearly and completely presented.

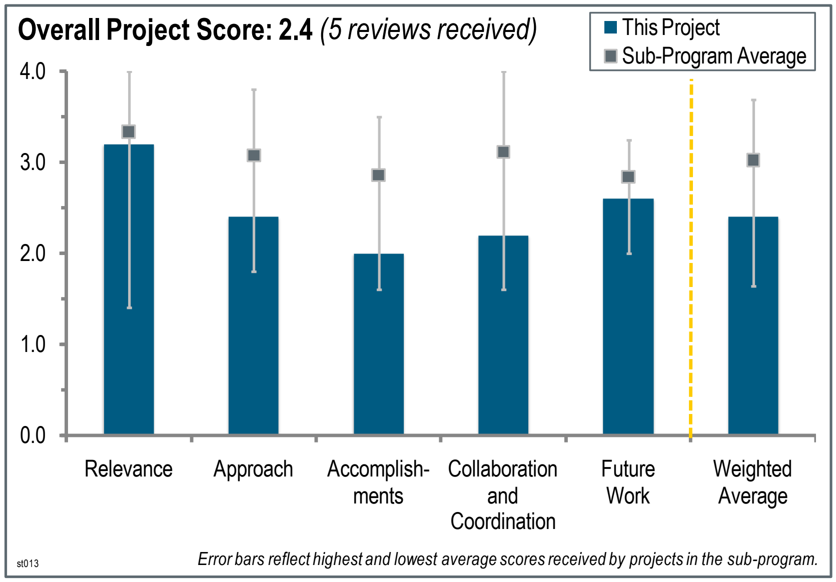
Recommendations for additions/deletions to project scope:

- The community needs a reason to believe sorbent type materials can meet the 2015 targets.

Project # ST-013: Composite Materials for Hazard Mitigation of Reactive Metal Hydrides

Joseph Pratt; Sandia National Laboratories

Brief Summary of Project:



Metal hydrides show promise for compact hydrogen storage, enabling hydrogen usage in diverse applications. However, some metal hydrides show unfavorable reactivity when exposed to air or water, such as in the event of an accident. A hazard mitigation strategy would help enable widespread use and commercialization of metal hydrides. The objective of the project is to develop a hazard mitigation strategy that, upon a breach in tank, would: (1) slow the reaction rate; (2) stop the penetration of oxygen; and/or (3) absorb the heat of the reaction. A composite mixture of the metal hydride with a polymer may have these mitigating features.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.2** for its relevance to U.S. Department of Energy (DOE) objectives.

- Metal hydrides show promise for compact hydrogen storage, enabling hydrogen usage in diverse applications. Understanding the behavior of hydrogen storage chemicals in an application environment will enable the design, handling, and operation of effective hydrogen storage systems for consumer applications.
- Risk mitigating solutions are relevant to hydrogen storage materials impacts, tank design, and meeting DOE targets.
- The project is relevant to DOE objectives, as it addresses important safety issues.
- The project concentrates almost entirely on the safety problem associated with air-reactive hydrides, and safety is an important component of DOE objectives. It is not clear whether sodium aluminum hydride ($NaAlH_4$) is the most important candidate hydride. Possible secondary objectives seem to be possible, but not recognized, e.g., the use of polymer coatings to reduce hydride poisoning from impure hydrogen.
- The relevance of complex hydride technology to DOE hydrogen storage objectives was evident with the clear introduction of technical gaps to be addressed as part of the project. Identification of hazard mitigation strategies for reactive metal hydrides that are important for achieving safety targets remains largely unexplored in the community.

Question 2: Approach to performing the work

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

- The major problem is that the content of the polymer in the hydride reduces the gravimetric hydrogen content significantly. It is unclear how diluting the hydride with inactive polymer will meet DOE's storage capacity goals. Further, it appears that cycling destroys protective properties of the polymer/hydride composite.
- For the relatively large budget allocated, the approach seems too limited. Only one polymer coating was tried, and then only one polymer system was included for future work. The rationale for initially choosing the polystyrene-divinylbenzene (PS-DVB) system is not very convincing.

- The approach is generally applicable to address barriers; however, the specific underlying purpose (mechanism of mitigation) for the composites remained somewhat unclear. It is additionally not apparent what the rationale for composite material selection and/or what the desired morphology (e.g., coating, dispersion, etc) was. The approach is a bit ad hoc in the current form.
- The project has significant weaknesses. It may have some impact on overcoming barriers.
- A composite materials approach might help, but its interaction with hydrogen storage material under heating might be hard to overcome.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.0** for its accomplishments and progress.

- Large-scale synthesis attempts were not justifiable, given that results showed polymer decomposition. More emphasis should have been placed on determining the stability of the hydride-matrix system in order to tailor and improve the system.
- Some progress in protecting from oxidation and water reactions has been shown for as-prepared composites. There is no clear path on how to address the stability of protective properties of composites during and after cycling. Suggestion of the potential of polystyrene-siloxane (PS-siloxane) appears to be not supported by experimental data, and it is unknown how stable these composites will be during and after cycling. The major problem is that there appears to be no understanding of how the composite acquires protective properties. Reproducibility of experiments appears to be an issue.
- The results of the PS-DVB systems are largely negative and this system has been only recently abandoned. The project is 90% completed; the reviewer asks why it took so long to abandon PS-DVB and move to PS-siloxane.
- Progress is appropriately focused on deducing processing-structure-property relationships for various composites involving $NaAlH_4$. Most of the important properties were assessed (e.g., capacity and response to cycling), although some additional structural characterization—for example, microstructure scanning electron microscopy analysis—would be beneficial. Clarification of the rationale for polymer selection (e.g., functional groups or backbone composition) is recommended.
- The project started in July 2007, but the progress to date appears to be very minimal.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.2** for its collaboration and coordination.

- The collaboration with the United Technologies Research Center (UTRC) should help the project.
- Collaboration is not visible apart from reactivity testing at UTRC. The project otherwise seems to be isolated.
- The role of UTRC is unclear.
- There is only one collaboration listed, which is with UTRC. There are other good hydride safety activities in the Hydrogen Storage Engineering Center of Excellence, Europe, and Japan, so it is unclear why there are not more collaborations.
- Collaboration with UTRC is mentioned; however, it is unclear what its role in this project is. Given the expertise and prior and current work of UTRC in formulating and characterizing metal hydride composites, it would be beneficial to strengthen this connection.

Question 5: Proposed future work

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

- Basically, future plans are continuation of work that has shown no useful results.
- There is very limited time left to the project (only 10%). Although the PS-siloxane approach is acceptable, it seems unlikely it will get very far toward practical feasibility. Other than rather vague "cross linking" arguments, it is not fully clear why PS-siloxane is the best choice for the remaining project work.

- In general, continuing the exploration of new, cross-linked polymer formulations is a relevant extension of current work, although it would be helpful to better understand why siloxane-based polymers are expected to be better than PS-DVB. Explanation of the underlying chemistry is encouraged.

Project strengths:

- The group is familiar in synthesizing polymer formulations such as polystyrene with siloxane cross linking, with and without siloxane moieties. The researchers successfully synthesized a metal hydride composite with copolymer PS-DVB, including differing cross-linking ratios.
- The project has made an attempt to address an important safety issue.
- The project is looking at an important safety objective.
- The project has strong relevance and is an important topic area for the metal hydride hydrogen storage materials class.

Project weaknesses:

- There is a lack of understanding of composite materials with better mitigating and stability properties, as shown by a polystyrene composite that initially mitigated heat release but was not robust enough to withstand charge/discharge cycling.
- The project is tailored toward complex metal hydrides only. The thermal stability of the polymer is an issue in the absence of the hydride. Higher stability systems need to be introduced.
- The research approach is fundamentally flawed, as it introduces too much of an inactive filler (polymer) into the composite. Little to no understanding of why the protection fails during cycling has been demonstrated.
- The project is limited in scope and has been largely unsuccessful so far.
- A better rationale for materials selection is needed.

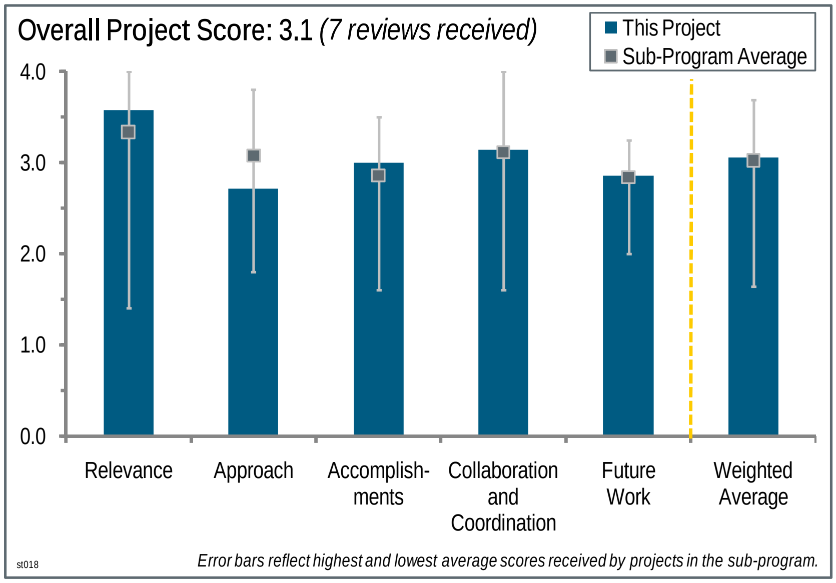
Recommendations for additions/deletions to project scope:

- The reviewer suggests the creation of go/no-go criteria if this project is to continue.
- It is recommended that this project is terminated in an orderly fashion.
- The project results are not commercially promising for this approach. It should not be continued with a new or renewed project after the current project expires in September 2011.

Project # ST-018: A Biomimetic Approach to Metal-Organic Frameworks with High H_2 Uptake

Joe Zhou; Texas A&M University

Brief Summary of Project:



The ultimate goal of this project is to prepare a metal-organic framework (MOF) with both high surface area and high hydrogen-affinity. Objectives for 2010 are to: (1) construct MOFs containing mesocavities with micro windows that may serve as a general approach toward stable MOFs with higher and higher surface areas; (2) incorporate entatic-state metal sites into the high-surface-area MOFs; (3) design and synthesize porous organic frameworks (POFs) for hydrogen storage with high surface areas, tunable pore size, and flexibility; and (4) determine the hydrogen adsorption level of POFs doped by metal, such as lithium and nickel. Milestones for 2011 are to: (1) construct porous polymer networks (PPNs) with an ultra high surface area; and (2) explore the possibility of incorporating charge and additional light metal ions such as lithium ion, sodium ion, or magnesium ion into PPN-4. The modified PPN-4 should have improved hydrogen affinity and improved volumetric hydrogen uptake due to the increased density.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.6** for its relevance to U.S. Department of Energy (DOE) objectives.

- The work was well presented, although it appears to be somewhat disjointed and more focused on increasing hydrogen binding at higher temperatures and less on surface area.
- The development of air- and moisture-stable hydrogen adsorption materials for room temperature application is very important overall to the DOE Hydrogen and Fuel Cells Program.
- This work is relevant to overall DOE objectives and was highlighted in the plenary reviews and overviews for successfully obtaining high weight percent physisorbed systems that have been published in high-profile journals. The project clearly supports the Program and the goals and objectives in the *Multi-Year Research, Development, and Demonstration Plan*.
- The project is directly aimed at meeting DOE objectives.
- The project is relevant because it addreses hydrogen storage targets.
- This project is focused on the development of ultra high surface area MOF materials with enhanced adsorption enthalpy and hydrogen physisorption capacity. The project supports DOE research and development objectives for improved materials for hydrogen storage. The approach is novel, and important new results have emerged that have established the benchmark for cryo-adsorbed material capacity.
- The project is aligned with the DOE hydrogen storage objectives and focuses on the discovery of new and improved sorbent materials with high capacity and increased heats of adsorption toward ambient temperature operation.

Question 2: Approach to performing the work

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

- The approach is focused on increasing hydrogen adsorption in MOFs and PPNs. Efforts appear to be directed at generating new MOFs and PPNs with high surface area, large cavities, and new functional groups that aid the incorporation of metal centers to increase the heat of hydrogen adsorption. The logic for deciding which functional groups or metal centers to include to increase the heat of adsorption is not presented. A pathway to increasing the heat of adsorption to the desired 15–30 kilojoules per mole is not apparent.
- An innovative approach is being used to synthesize functionalized MOFs and PPN structures with ultra high surface area to facilitate enhanced hydrogen storage capacity and increased hydrogen binding energy compared to other MOFs and open framework structures. The motivation for the task on enhanced hydrogen adsorption via electrostatic interactions (charge separation) in porous framework structures is intuitively appealing. However, the expected magnitude of the electrostatic field strength compared to the energy needed to promote enhanced adsorption by an induced dipole-surface interaction energy has not been estimated or simulated, and the proposed approach for studying the effect is not defined in sufficient detail to allow a critical evaluation to be made.
- The approach generally concerns two thrusts: increasing surface area and increasing binding enthalpy. The latter approach of enhanced binding is appropriate and being investigated through a variety of unique strategies including linker functionalization and metal incorporation, although these efforts could improve in the way of focus. The approach of increasing surface area does not address (and even is at odds) with a critical barrier for sorbent materials concerning improving volumetric storage capacity. It appears that the goal of reaching the highest surface area or gravimetric capacity is taking a priority to the rational design and creation of sorbent materials, which are optimized for volumetric capacity (as well as gravimetric capacity).
- The high surface area and improved heat of adsorption approaches are good in general. When working on both approaches in parallel paths, it is very critical to keep them balanced for overall achievement. The theory directed experimental approach is also very good.
- The approach to performing the work is good, but falls short of the very high standards of other related projects. The project is, however, well designed, feasible, and integrated with other efforts.
- The project has a multiprong approach to developing high-capacity physisorption hydrogen storage materials.
- The project is lacking a rational design regarding the types of materials that are being pursued for synthesis. Much of the work is derivative of others in the field, and more focus is suggested.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The project is around 85% complete and is on target to finish on the end date of June 30, 2012. Full characterization on a number of key systems has been performed and the relevance and high academic standard of this work with publications of exceptional quality are evidenced by publications in *Science* (2010, 329, 424) and *Nature Chemistry* (2010, 2, 944).
- PPN-4 silicon has recorded a high Brunauer-Emmett-Teller (BET) surface area of 6,470 square meters per gram (m^2/g). The gravimetric excess hydrogen uptake of PPN-4 silicon was 8.5 weight percent at 77 kelvin (K) and 60.4 bar. This is a new benchmark for physisorption materials at 77 K. This material is stable in air and moisture and can be compressed without losing its porosity. There does not seem to have been much progress on MOFs compared to past years. The focus now appears to be on developing new PPNs.
- The project has increased hydrogen adsorption in MOFs and PPNs at 77 K, but the researhers have been relatively unsuccessful at increasing the heat of adsorption to the desired range and increasing hydrogen adsorption at higher temperatures. From the results shown, the majority of the effort appears to have been directed at creating new MOFs and PPNs and higher surface areas. There appears to have been little effort at incorporating metal centers into the MOFs and PPNs. Data showing incorporation of lithium centers into PPNs is limited.
- Impressive results have been obtained on high-surface-area, high-capacity porous framework materials. Most noteworthy are the results obtained in substituted PPN compounds with high stability. A BET surface area in excess of 6,450 m^2/g and gravimetric capacity of 8.5% at 77 K and 60 bar were measured and validated (Southwest Research Institute). Moreover, the material seems to be thermally stable and relatively insensitive to

degradation by water exposure. These are important "benchmark results" that make these materials top contenders for incorporation into an operational cryo-adsorption system. However, there may be some confusion about the capacity (volumetric and gravimetric) because even though the material is amorphous or subcrystalline, the density calculations are based on the assumption of a crystalline unit cell. That discrepancy should be resolved in future work.
- The progress is generally adequate and, indeed, many new impressive MOFs have been discovered and their hydrogen storage properties have been assessed. The calculation of volumetric capacity should be based on bulk (tapped) density in addition to the more unrealistic single crystal values and compared with other data for benchmark materials in the sorbent area. The calculation based on a compressed sample of PPN-4 should be for an actual compacted sample of known density that had its uptake measured. The current projections are not only confusing but seem unrealistic based on the given values for "single crystal density" (which again, seem to be unknown).
- A large number of systems have been examined, and it is clear that the project team is producing large numbers of materials.
- The researchers accomplished a benchmark on the polymer-based porous materials. While trying to improve the surface area, the principal investigator (PI) should also consider the volumetric-based storage by increasing the density at the same time.

Question 4: Collaboration and coordination with other institutions

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

- There has not been as much collaboration inside the Hydrogen Storage sub-program as there could be.
- There are only limited numbers of the group willing to send out their samples for others to validate results. This one is definitely a top one on the list.
- The group has both national and international collaborators who, though not necessarily internationally leading, are nevertheless making a very substantial contribution to the project. The collaborative nature of the project is well formed.
- There are strong collaborations and validation of results.
- There are many collaborations in this project. It is not clear what theoretical calculations are being performed and how they are influencing the project. Theoretical estimates of how much the heat of adsorption can be improved by incorporating metal atoms would be beneficial.
- There is good collaboration between the Texas A&M group and theorists and experimentalists at a variety of universities, government laboratories, and industry laboratories. Although these collaborations have been beneficial, it is very important for the PI to become more actively engaged with the Hydrogen Storage Engineering Center of Excellence (HSECoE) partners, especially the Jet Propulsion Laboratory and the adsorption technology team within the HSECoE. Guidance from the partners on adsorption system needs and requirements would undoubtedly enhance the overall impact of this project.
- Validation of samples and collaborations appear to be well established and complement the work being done. It might be useful to be in communication with the HSECoE for the more developed materials coming out of this work.

Question 5: Proposed future work

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

- The project has effectively planned its future in a logical manner and has incorporated appropriate decision points. With around one year remaining in the project, adequate consideration has been made to barriers and risk mitigation. The proposed future work is commensurate with the end date of June 30, 2012.
- Future work is appropriate, but a down-selecting of work between MOFs and PPNs might be appropriate.
- Work preparing more MOFs with high surface area should be curtailed, and instead the team should focus on incorporating metal atoms or ions in the existing MOF and PPN structures and demonstrating that incorporating the metal can increase the heat of adsorption to the range needed.
- Future work on PPNs and functional MOFS is a direct extension of the 2010–2011 effort. However, potential obstacles and technology hurdles have not been presented or discussed, so it is difficult to assess how the future work should be prioritized. The PI is encouraged to carefully evaluate risks and technology challenges, propose mitigation strategies, and adjust the focus of the future effort accordingly. Metal incorporation and introduction

of charge separation centers into porous framework structures are potentially important areas for future work. However, a good technical rationale based on more complete simulation and modeling studies would be helpful (especially in the case of charge separation, where relative electrostatic field energies and energies for induced dipole interactions should be compared). Likewise, effects of impurity “poisoning” of reactive sites on the hydrogen adsorption yield should be carefully considered.
- Overall, the future work is a logical extension of current progress; however, additional emphasis should be placed on volumetric capacity. In the future work’s current form, the PI appears to be more focused on a continued emphasis of pushing surface area and gravimetric uptake records that do not help volumetric capacity.
- The future plan sounds good in general. There is not a clear path on how to balance the volumetric and gravimatic-based hydrogen capacity.

Project strengths:

- The theory-guided experimental work is very important for a bottom-up designed material. Another strong point of this project is the measurement validation. The PI is very cautious about reporting a breakthrough milestone. All of the results are independantly validated.
- The work is of a high academic standard with publications of exceptional quality.
- There are good collaborations with national laboratories, other universities, and industry.
- The project has strong synthetic skills, analytical tools, and techniques.
- A novel and innovative experimental approach is being employed to synthesize porous framework structures for high-capacity cryo-adsorption. The PI and his team have extensive experience in synthesis and testing of those materials.
- The project has a capable team with great synthetic skills.
- The PI is a good researcher.

Project weaknesses:

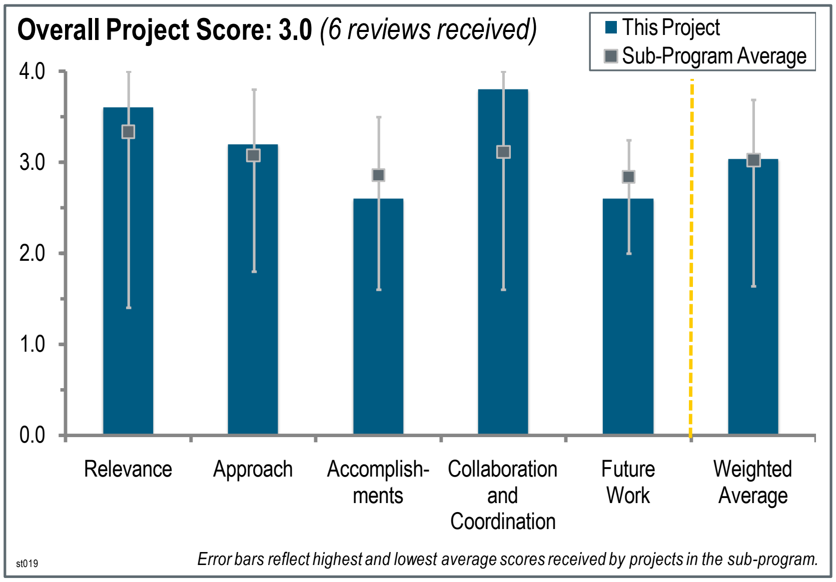
- It is not clear how to achieve the balance between improved surface area and improved heat of adsorption approaches. There must be a optimized value or target for the PI.
- The project is of a high quality, but perhaps lacks the leading edge innovation of non-U.S. groups in MOFs and other U.S. groups in covalent-organic framework and polyoxometallate work. Several inconsistencies were identified in the work during the oral questioning after the presentation that suggest a certain lack of rigor with the analysis. This was particularly evident in a discussion of the porosity of PPN-4 (simulated versus experimental). The degree of computational support could be stronger.
- A more thorough evaluation (supported by measurements) of the stability issues of MOFs should be in the presentation.
- Contributions of the theoretical calculations are not apparent. Focus needs to be on improving heat of adsorption, not on preparing MOFs or PPNs with better adsorption at 77 K.
- A more robust collaboration between the Texas A&M team and the HSECoE is needed. Only very limited information is provided concerning the role that charge separation centers will play in the formation of internal electrostatic fields. A more rigorous treatment of charge separation effects and the magnitude of the associated electrostatic fields is needed to establish a solid rationale for continuing work on enhanced adsorption due to induced dipole effects.
- There is a need to strengthen focus on volumetric capacity.
- The project needs more focus.

Recommendations for additions/deletions to project scope:

- It will be beneficial if the PI can add some modeling work to predict the balance of improved surface area and improved heat of adsorption based on what the team has already learned.
- MOF development could be aided by modeling methods developed by other groups. More clarification on volumetric energy storage density is needed.
- A more focused effort on exploring ways to increase the adsorption enthalpy is recommended. Closer collaboration between this project and the HSECoE is strongly encouraged.

Project # ST-019: Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

Peter Pfeifer; University of Missouri



Brief Summary of Project:

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

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.6** for its relevance to U.S. Department of Energy (DOE) objectives.

- This approach to high-surface-area carbon has significant possibilities for the Hydrogen Storage sub-program. The reviewer suggests that these materials should be shared with other storage groups, specifically the Hydrogen Storage Engineering Center of Excellence (HSECoE), which is having trouble getting high-surface-area activated carbon adsorbents, AX-21, and other materials.
- This work is very relevant to overall DOE objectives; the research is meticulous and the large briquettes show attention to the requirement of transferring scientific discovery to technology development. The project clearly supports the DOE Hydrogen and Fuel Cells Program.
- The project is relevant to DOE objectives, in particular reducing the raw materials cost of hydrogen storage materials.
- This project correctly targets development of novel materials that will overcome both the low volumetric hydrogen densities and hydrogen binding energies that currently preclude the practical utilization of nanoporous materials as onboard hydrogen storage materials at ambient temperatures.
- The project addresses hydrogen storage goals and targets.
- The development of low-cost hydrogen storage materials for room temperature storage is highly relevant.

Question 2: Approach to performing the work

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

- The approach to performing the work is methodical and of a very high quality. There is a deep understanding of surface-functionalized nanoporous carbon. Work has been carefully undertaken and there has, for example, been an accurate validation between the project’s hydrogen test fixture and the Hiden hydrogen sorption analyser equipment. The project is well designed, feasible, and integrated with other efforts both nationally and internationally.
- The work this year had focused on fundamental measurements and modeling. However, the experimental results (reduced capacities at 90 kelvin [K] with boron-doping) do not seem to justify the fundamental modeling work at this time. Rather, there should be more modeling focused on improving the properties of the materials. The engineering scale test bed and testing is something that should come later or be done by the HSECoE.

- The approach of boron-doping the nanoporous carbon to increase the hydrogen binding enthalpies is reasonable. However, there seems to be no model for predicting how much additional stability will be or can be gained through this approach, and no reason to believe that this approach would ever lead to materials with room temperature stabilities. Similarly, the approaches to improving the volumetric hydrogen densities are sound, but do not seem likely that they will provide enough improvement to meet the Program targets.
- The project approach is to increase hydrogen adsorption on carbon via optimization of pore geometry and doping the carbon with boron and lithium. The project has a unique approach to utilize boron doping and boron neutron capture. Ab initio calculations and experiments indicate boron-doping can increase the hydrogen adsorption energy.
- The approach to develop high-surface-area, functionalized carbon-based hydrogen storage materials from inexpensive precursors such as corncob is excellent. There is emphasis on room temperature hydrogen storage.
- This work is clearly well thought-out and executed.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The project has made good progress in materials synthesis.
- The project is around 60% complete and is on target to finish on the end date of January 31, 2013. Technical accomplishments include optimisation of pore geometry and the observation of boron-carbon bonds by Fourier transform infrared spectroscopy. The project has correctly stopped a number of tasks.
- The project has made limited improvement in materials properties compared to overall work performed. There does not seem to have been as much focus as in the prior year on evaluating changes in heat of adsorption with the new formulation for boron-doped carbons.
- Good progress has been made in the synthesis and testing of the boron-doped materials and in the determination of the volumetric hydrogen density of compressed monoliths. Unfortunately, the values determined fall far short of the Program targets.
- The project demonstrated an increase in the hydrogen adsorption energy via boron-doping. The project has increased room temperature storage in a monolith to 2.5 weight percent (wt%) and 9.5 grams per liter (g/L) at a pressure of 100 bar. There is progress, but still far below targets.
- Boron-doping has shown a 30% increase in room temperature gravimetric hydrogen storage capacity. The briquette results have produced volumetric hydrogen storage capacities as high as 10 g/L at 100 bar.

Question 4: Collaboration and coordination with other institutions

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

- The reviewer suggests a stronger connection to HSECoE.
- The group has both national and international collaborators who make a very substantial contribution to the project. The collaborative nature of the project is well formed. The group also has unique facilities that it is keen to share with other DOE projects.
- Validation testing with the National Renewable Energy Laboratory was an important step. The project has good collaborations on modeling and fundamental measurements. Scale-up work could be done by, or at least in collaboration with, HSECoE.
- The project has excellent collaborations, including a quality partner for measurement validation.
- The collaboration with modelers is productive.
- A large number of collaborations appear to be producing useful information.

Question 5: Proposed future work

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

- The monolith work will be very important.
- After several no-go decisions, the project has effectively planned its future in a logical manner and has incorporated appropriate decision points. With around 1.5 years remaining, adequate consideration has been

made to barriers and risk mitigation. The proposed future work is commensurate with the end date of June 30, 2012.
- The plan for materials development and improvement is good. Given the "Chahine rule" capacity limitation, the focus on increased surface area and increased enthalpies of adsorption are critical to the success of the project and should, therefore, be the main focus.
- The is no path forward to raise hydrogen binding energies above 11 kilojoules per mole and volumetric hydrogen density above 10 g/L.
- Proposed future work is logical and addresses the key questions about the isosteric heat of adsorption of boron-doped samples and how the heat of adsorption varies with boron-doping and hydrogen coverage.
- Future work should continue and build on current activities.

Project strengths:

- The project is well thought-out and has careful analysis.
- The work is of a high engineering and technical standard.
- The group has the ability to produce and characterize modified physisorption materials. The materials synthesis and modification approach seems to be scalable and potentially less costly than other technologies.
- The project has a highly competent team of experimentalists.
- There is a good mix of modeling and experiment.
- The project targets a low-cost material for room temperature hydrogen storage.

Project weaknesses:

- The project is of a high quality, although the long list of publications is less significant given the lack of high-profile publications. A number of original tasks have been stopped or not started, indicating perhaps an initial lack of clarity about the direction of the project.
- There is not enough progress on developing materials with significantly better properties than commercial activated carbons.
- The approaches seem to have little chance of meeting Program targets.
- Room temperature gravimetric hydrogen storage capacities are still below 1 wt%, and there does not appear to be a breakthrough strategy for significant improvements.

Recommendations for additions/deletions to project scope:

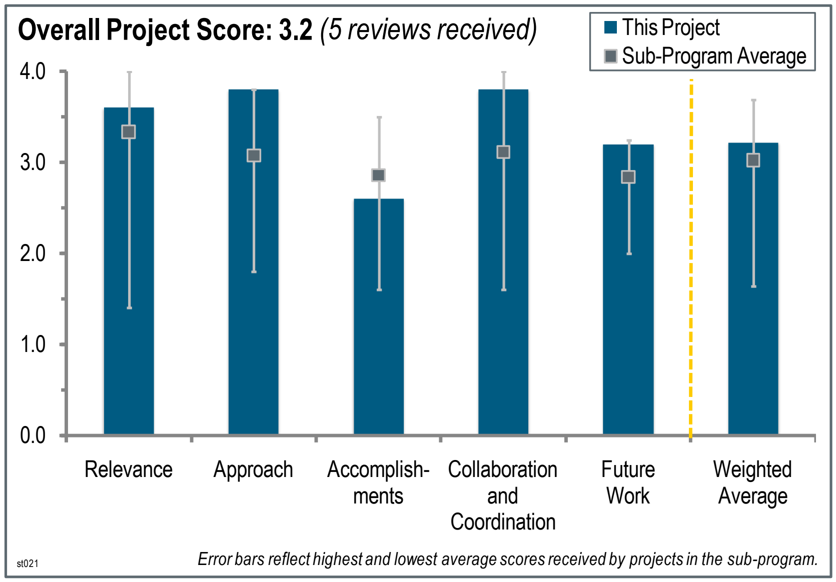
- The project should coordinate with HSECoE on scale-up and monolith testing.

Project # ST-021: Weak Chemisorption Validation

Thomas Gennett; National Renewable Energy Laboratory

Brief Summary of Project:

The overall objective of this project is to evaluate the hydrogen spillover mechanism as a means to achieve the U.S. Department of Energy's (DOE's) 2015 hydrogen storage goals. The goals of the project include: (1) validation of measurement methods, including reproducibility and round-robin measurements of standards at several sites; (2) identification and synthesis of several candidate sorbents for spillover; (3) determination of hydrogen sorption capacity enhancement from spillover; and (4) observation and characterization of spillover hydrogen-substrate interactions with spectroscopic techniques.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.6** for its relevance to DOE objectives.

- An analysis of the critical question about the importance of spillover is overdue. This is an important open question that should have been addressed in the Hydrogen Sorption Center of Excellence work.
- This project is extremely important to the Hydrogen Storage sub-program, which has an objective to establish whether the "hydrogen spillover" process can be regarded as a viable approach for improving the reversible storage capacity at ambient temperature. Its goal is to determine whether enhanced amounts of hydrogen can be transferred from the gas onto or into carbon-based adsorbent via metal catalysts. In particular, it seeks reproducibility of the spillover mechanism from measurements performed at independent laboratories on common samples that have been purported to exhibit this behavior. Furthermore, spectroscopic methods would be used in attempts to verify whether any "unique" hydrogen bonding with the host materials can be attributed to spillover.
- Validation of measurement methods for reproducible results is a very important part of the DOE Hydrogen and Fuel Cells Program.
- This work is relevant to overall DOE objectives. DOE wishes to understand spillover, and this is the organized project that should deliver results.

Question 2: Approach to performing the work

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

- It is a good start to narrow down analysis to a few reproducable samples. The project uses a good approach of having multiple groups and approaches provide semi-quantitative analyses for the role of spillover to determine if this is a minor phenomenon or an important outcome to enhance hydrogen storage on sorbents.
- The National Renewable Energy Laboratory has gathered together a diverse team to prepare and characterize adsorbent materials previously reported to have exhibited at least a 15% increase in hydrogen storage capacity from the spillover process. Independent measurements of capacities will be made on common samples while infrared (IR), neutron scattering, and nuclear magnetic resonance (NMR) techniques will probe for specific

signatures of hydrogen-substrate interactions. Outside testing and reviews of the observations made by the core team will also be included during periodic meetings over the course of this project.
- Calibrating the instruments and round-robin tests are a really good effort.
- Great attention and consideration has been given to this experimentally difficult project. The project is well designed with a good balance between experiment and analysis; the project is feasible and its round-robin nature is essential.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The project is just starting and appears to be at the beginning of a good plan.
- About eight months into this project, reference and spillover exhibiting materials have been made and partially characterized for hydrogen capacities and IR spectra. However, the round-robin exchange is apparently behind schedule, awaiting verification of key properties. Furthermore, there have been delays in completing subcontracts. This has had significant impacts on setting up and performing some key tasks (e.g., NMR studies). Looking at the situation as of May 2011, it seems highly unlikely that project milestones can be completed by the schedule shown on slide 10 of the presentation. Slippage of several months will be necessary to complete the proposed experiments before detailed comparisons can be made.
- A diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) investigation of spillover hydrogen showed very interesting results. It would be good to compare the DRIFTS investigation on a low platinum loading sample (1–5 weight percent [wt%] sample rather than the 40 wt% platinum sample only).
- The project has achieved a number of very good accomplishments, but there is still a substantial degree of uncertainty. This is not because of a lack of capability of the project members (they are internationally recognized), but as a consequence of the difficulty of the subject.

Question 4: Collaboration and coordination with other institutions

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

- Angela Luekinig at Pennylsvania State University did some nice work to find a sample that stood out from the rest that shows increased probability for “excess” adsorption. This reviewer asks if it is too late to consider this material.
- This project involves highly qualified experimental research groups that should be able to make the desired assessments. It appears that coordination of supplying materials for the round-robin and the spectroscopic tests is much more complex and taking longer than initially believed. There appears to be common purpose and strong desire among the partner organizations to perform their tasks.
- There is excellent collaboration among multiple players.
- The project is an excellent example of collaboration, a round-robin analysis between internationally leading groups that collaborate effectively is the best way to handle this project.
- The project has a very strong team.

Question 5: Proposed future work

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

- Previous theoretical studies must have provided insight into potential vibrational modes, but it was not clear if these past results are being used to direct where to look in the details of the DRIFTS data. If neutron scattering data is collected at temperatures below 77 Kelvin, it is not clear why IR or Raman spectroscopy cannot be measured at lower temperatures. There must be conditions where samples can be prepared where physi-sorption is not an issue. The hydrogen NMR could provide dynamics information on deuterium-covered samples to be compared with inelastic neutron scattering experiments. This could provide some insight into carbon-deuterium bonding. Also, experiments using deuterium hydride gas could be used to look for Kubas type interactions by NMR spectroscopy. The reviewer asks if there is hydrogen activation at defect sites.

- The devised plan for the task is quite clear, and contributions expected from the individual groups have been identified. Conducting the specific experiments and analysis should be possible; however, it will almost certainly take significantly longer than originally intended.
- The demonstration of spectroscopic evidence for spillover through carbon-hydrogen bonds is very important for the community to fully understand the mechanism of the spillover effort.
- The project has the limited objective of assessing the basics of spillover and should accomplish this at the end of the project. If positive results are achieved, then a follow-on project involving this collaboration is encouraged. The end of this project may just be the beginning of the understanding of spillover. A future project between the project members is encouraged.

Project strengths:

- The project has a good team comprising people asking the right questions.
- A diverse group of very competent researchers have been assembled to prepare and characterize these materials to see if spillover does occur at some level. Having round-robin testing of hydrogen capacities complemented by the selected spectroscopic techniques could establish the extent and reproducibility of spillover.
- The reviewer detected no major flaws in the planned activities.
- A project strength is the round-robin tests and experimental method validation.
- The work is methodical and carefully undertaken.

Project weaknesses:

- There is concern whether three "signatures" is sufficient.
- The logistics of preparing and validating reference and spillover samples to send to organizations located around the world has proven much more challenging and is impeding progress. Comparing results from different laboratories using variable procedures is tedious and potentially contentious. Furthermore, unequivocal evidence for spillover species may not be identified from the chosen spectroscopic methods, although they are probably the best options at this time.
- It will be really helpful if the principal investigator (PI) could identify a path to seperate the direct chemisorption of hydrogen on metal from the total hydrogen capacity measurement.
- Spillover is a very difficult subject in which to derive accurate data and information. The project is fraught with uncertainties.

Recommendations for additions/deletions to project scope:

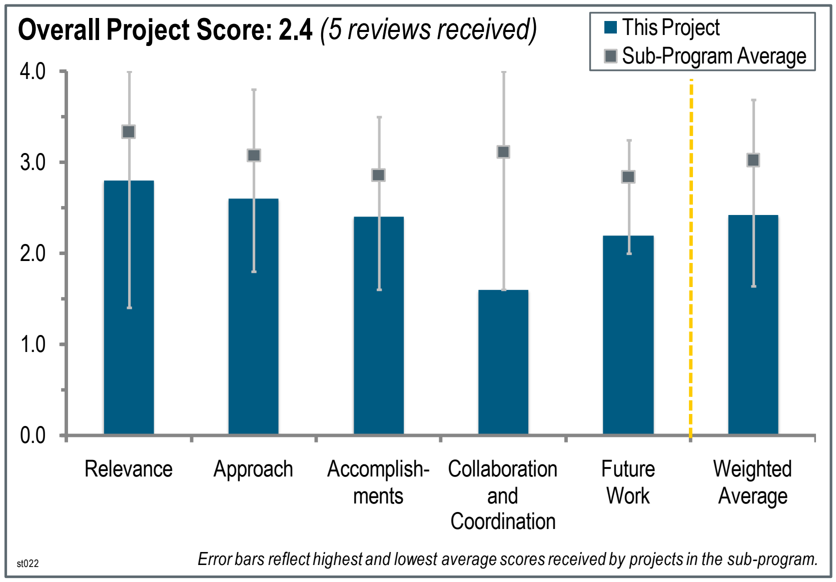
- The reviewer urges DOE to support this effort through the planned activities (i.e., tasks described on slides 19 and 20 of the presentation) either by no-cost extensions or some additional funding until the research groups can complete assessment of at least two of the proposed materials from round-robin capacity testing and spectroscopic measurements. It would be most unfortunate to leave the issue of hydrogen spillover dangling. The PI needs to manage the efforts of different teams and keep them focused on completing their assigned tasks efficiently and accurately. All reports within and between the teams should provide full disclosure of any problems, failures, etc., so that consensus can be achieved without regard for the consequences.
- The researchers should consider increasing the project scope and either extending the existing project or beginning a follow-on project.

Project # ST-022: A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs/ZIFs for Onboard Vehicular Hydrogen Storage

Omar Yaghi; Universityof California, Los Angeles

Brief Summary of Project:

The overall objective of this project is to achieve room temperature hydrogen storage in covalent organic frameworks (COFs) to meet the U.S. Department of Energy's (DOE's) 2015 targets. Objectives for fiscal years 2010–2011 are to: (1) design new COFs with strong hydrogen binding sites; (2) predict hydrogen uptake isotherm for designed frameworks with developed Force Field; (3) prepare stable frameworks with potential metal binding sites; (4) implement metalation experiments and evaluate the hydrogen adsorption property; and (5) prepare mixed-metal zeolitic imidazolate frameworks (ZIFs).



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **2.8** for its relevance to DOE objectives.

- This project is of relevance to DOE Hydrogen and Fuel Cells Program objectives only in the broad sense that it is based on the premise that introduction of pendent metal complexes to COFs could result in materials with greater hydrogen binding energies. However, a project that targets the production of materials that will have unacceptably high costs and unacceptable gravimetric densities is of little relevance to Program targets and goals.
- Improving the stability of porous materials for hydrogen storage is an important goal. Thus, the emphasis on COFs is to be applauded. In addition, the approach to increasing the surface density of metal sites to increase the hydrogen capacity at high temperature seems well considered. Unfortunately, the focus has been on the precious metals palladium and platinum, which are expensive. Moreover, there was no scientific reason given for these choices, as it seems that the first row transition metals or alkali metals should work better.
- The project focuses on modeling and synthesis of porous COFs and ZIFs for enhanced binding of physisorbed hydrogen. The discovery of improved high-porosity physisorption media is an important research thrust that supports the Program goals. A primary objective is to increase hydrogen adsorption energies without losing pore volume in COFs by controllably incorporating binding centers. It is also focusing on the synthesis of mixed metal ZIFs, which may show enhanced adsorption enthalpy. These research and development activities are relevant to the DOE research, development, and demonstration objectives for improved hydrogen storage materials.
- The project is investigating totally new classes of materials for hydrogen storage.
- The project work is relevant to most of DOE's storage mission.

Question 2: Approach to performing the work

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

- The reviewer asks what the high-throughput approach is for discovery. The reviewer also asks if the researchers are incorporating noble metals and questions why the projected materials will improve properties.

- In addition to the flaws of adding unacceptably high cost in the cases of the pendent platinum chloride ($PtCl_2$) and palladium chloride ($PdCl_2$) groups and lowering gravimetric densities to unacceptable values in the cases of the pendent $PtCl_2$, $PdCl_2$, and ferrocene groups, the approach of adding metal complexes that will not directly coordinate molecular hydrogen is off target.
- The approach to the synthesis work is excellent and the emphasis on more stable COFs and incorporating metal sites is good. However, the computations are not state-of-the-art or particularly useful.
- The approach involves a combination of theory and simulation and synthesis work to fabricate porous COFs and ZIFs for enhanced hydrogen binding. The approach is logical and straightforward. However, the advantages of COF and ZIF structures compared to more conventional metal-organic frameworks (MOFs) are not stated clearly. Consequently, the overall motivation for the work is not particularly compelling. Likewise, the statement that "high throughput material discovery is applicable" is supposedly intended to describe an important feature of the approach. However, the high-throughput aspects of the approach are not readily apparent from the work presented. Also, in other systems (mainly organometallic systems), platinum and palladium have not shown enhanced binding behavior. The reviewer wonders if there is a solid reason to believe that those metals will be advantageous.
- The approach of adding higher-binding-enthalpy hydrogen-metal sites to the new classes of materials being synthesized is excellent.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.4** for its accomplishments and progress.

- The reviewer is not convinced that the measurement techniques are accurate and questions if they have been validated. The presenters did not demonstrate convincing arguments as to why new projected materials will be useful in improving binding energy. The chemistry and ability to make a variety of materials is strong.
- New COFs were synthesized and some highly suspect calculations were carried out to support the premise that addition of pendent $PtCl_2$, $PdCl_2$, and ferrocene groups will somehow increase the hydrogen binding energies.
- The odd behavior of the isosteric heat of adsorption at low loading for COF-43 and the lower than expected hydrogen loadings based on the surface areas suggests that they are likely not fully activated. The development of metallized COFs and strategies for creating more is excellent. They must work to overcome the reduced surface area and move away from precious metals. More work needs to be done to determine the structures of the metallized versions of COF-301.
- Several "proposed target structures" containing enhanced binding centers have been identified from modeling studies, and synthesis is underway. It remains to be seen whether the metal reactive binding sites can be incorporated into the COFs, and whether they actually facilitate enhanced binding. The work on simulation of the effects of partial metalation or mixed metal impregnation on the delivery amount of hydrogen is very useful, and it should provide important information to guide the synthesis effort. The density of metal sites predicted for the metalated COFs is an important quantity. However, only very limited information about the metal density has been provided.
- A number of avenues for metal binding sites are being developed. The observation that palladium metal site additions to COF-301 actually decreased hydrogen uptake at 77 kelvin as compared to undoped COF-301 is a bit discouraging.

Question 4: Collaboration and coordination with other institutions

This project was rated **1.6** for its collaboration and coordination.

- The project has had almost no collaborations, and there has been no validation.
- The mandatory "collaborators" slide was not included in the presentation, so it hard to evaluate the collaborations. However, it appears that the collaboration with BASF awaits an initial demonstration that the materials will have the targeted properties, which this reviewer thinks is unlikely.
- The primary collaboration seems to be with BASF on isotherm measurements. Because the calculations are not state-of-the-art, the researchers should develop new collaborations to provide this input into their synthetic project.

- Collaborations with university partners in “organic synthesis and material design” and with BASF on “verification” are mentioned in the presentation. However, the specific contributions of collaborators are not evident from the presentation. No DOE collaborators are included.
- The primary collaboration is with BASF. However, this project would benefit from collaborations associated with the introduction of non-precious metals into the COFs and ZIFs.

Question 5: Proposed future work

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

- It is not clear why next-generation materials will have improved performance.
- There is no clear path forward to producing materials that meet targets of adequate hydrogen binding energies and volumetric densities.
- The emphasis on metallization of the COFs should continue, and the computational project should be curtailed.
- The future plans primarily involve the synthesis and testing of material structures derived from the simulation work. An important focus is on the incorporation of reactive metal centers in the porous structures. At this stage of the project it is important to focus on a prototype structure that can serve as a “proof of concept” demonstration. Technology hurdles and barriers are not described. It is important to identify potential problem areas and suggest ways to ameliorate those problems. The reviewer asks, for example, if poisoning of the metal sites by reactive impurities is a potential problem.
- The emphasis of future work must be to identify a metal binding site addition that markedly increases hydrogen storage uptake.

Project strengths:

- The project has very good synthesis techniques and can create a variety of different structures.
- The principal investigator (PI) is a world leader in the design and synthesis of nanoporous materials.
- The project has excellent synthetic strategies (except for the use of palladium and platinum). There is an exceptional record of accomplishment in the synthesis of this and related classes of materials.
- The University of California, Los Angeles investigators are known experts in the synthesis and characterization of porous framework structures. This is a well formulated, broad-based project comprising a systematic approach focused on novel material discovery.
- The project has superb materials synthesis and chemistry.

Project weaknesses:

- The work does not seem to have significantly advanced toward improved hydrogen storage. There was insufficient data to show stability in air. The researchers should be more concerned about volumetric capacity.
- The PI is not focusing on developing materials that will meet DOE targets.
- Project calculations are not state-of-the-art.
- The advantages of COF and ZIF structures over existing MOFs are not evident. Likewise, a compelling motivation for the work based on either theory or experiment is not readily apparent.
- Emphasis appears to be on precious metal additions.

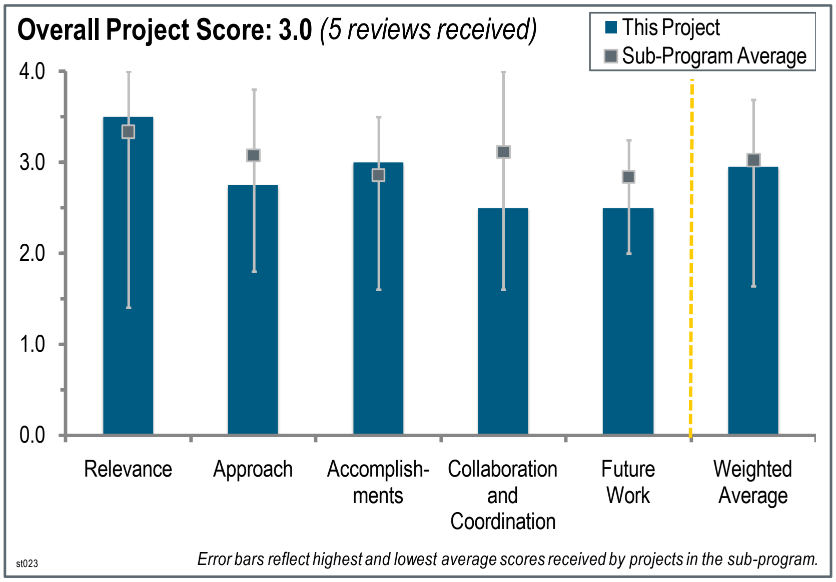
Recommendations for additions/deletions to project scope:

- The researchers need to be certain that all measurements are accurate via external validation. The reviewer does not consider the progress to be commensurate with the funding level.
- More emphasis on high-throughput synthetic methods would be welcome. The computational project should be curtailed.
- It is recommended that the project focus on the synthesis of a prototype system containing reactive metal centers that can serve as a demonstration vehicle upon which future work can be built.
- Recently, Los Alamos National Laboratory (LANL) developed some very interesting non-precious-metal catalyst materials. Collaboration with LANL in this area might be highly beneficial.

Project # ST-023: New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

Randy Snurr; Northwestern University

Brief Summary of Project:



The overall objective of this project is to develop new materials to meet the U.S. Department of Energy's (DOE) volumetric and gravimetric targets for hydrogen storage, including metal-organic frameworks (MOFs) and polymer organic frameworks (POFs). The researchers believe that hydrogen storage sorbents must have both high heats of adsorption and high surface area. The objectives for the current year are to: (1) develop MOF and POF materials with very high surface area and containing functional groups that can bind hydrogen; (2) measure heats of adsorption and hydrogen uptake; (3) use modeling to aid in the development of high-surface-area materials and develop models for cation-containing MOFs; and (4) screen different cations and cation environments for their ability to bind hydrogen and the resulting storage capacities.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.5** for its relevance to DOE objectives.

- The development of hydrogen storage materials with high heats of adsorption and high surface area for near-room temperature application is very important for automotive application.
- This work is relevant to the overall DOE objectives and was highlighted in the plenary reviews and overviews for successfully obtaining high weight percent (wt%) of physisorbed systems that have been published in high-profile journals such as *Nature Chemistry*. The project clearly supports the DOE Hydrogen and Fuel Cells Program and the goals and objectives in the DOE Office of Renewable Energy and Energy Efficiency, Fuel Cell Technologies Program *Multi-Year Research, Development and Demonstration Plan*.
- Project personnel are aware of the DOE goals and needs. The work is relevant to DOE targets.
- The project is addressing increasing surface area and heats of adsorption of physisorption storage materials, which is relevant to DOE objectives.
- This project targets the synthesis of novel nanoporous materials that have hydrogen binding energies that will allow them to be used for hydrogen storage at ambient temperatures, overcoming at least one of the barriers to the practical application of nanoporous materials in onboard hydrogen storage. The relevance of the project is lacking due to the insufficient attention paid to the barrier of inadequate volumetric hydrogen densities.

Question 2: Approach to performing the work

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

- The theory-guided experimental design is a very important and efficient approach.
- The project has achieved a number of outstanding accomplishments that include an achieved material gravimetric capacity of > 6 wt% at 77 kelvin (K) and 100 bar and a material volumetric capacity of > 30 grams per liter at 77 K and 100 bar. Other key milestones include synthesized POFs with surface areas of > 1,500

square meters per gram and 10 kilojoules per mole heat of adsorption with little or no drop-off at higher coverages.
- Heat of adsorption and surface area are both important. The teamed approach is good. The reviewer asks if in a comparison between cations and zwitterions, if cations will really be better. Low coverage data for higher heats of adsorption exists, but the reviewer wants to know what happens at high coverage.
- The focus appears to be more directly aimed at using modeling to support directions for materials development.
- The approach of the addition of metals to nanoporous materials to increase the hydrogen binding enthalpies is reasonable. However, there seems to be no model for predicting how much additional stability will be gained through the metal interaction and no evidence provided to support that this approach will lead to materials with room temperature stabilities.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The modified supercritical drying process is well adapted to the MOF activation process. The new project-developed MOF, NU-100, sets a new hydrogen capacity benchmark for the MOF-based hydrogen storage materials.
- The project is an excellent example of collaboration that is compact with a small number of internationally leading groups that collaborate effectively with highly complementary capabilities.
- The porous organic polymers synthesis with high surface area is good. The project is reporting mostly cryogenic results but claiming improved binding energy for cations. The reviewer questions this. There is good computation. The reviewer is concerned that a cation approach will not really lead to higher room temperature storage.
- The approach to developing new MOFs appears to be working. The researchers performed high-pressure 77 K measurements that were missing in past work, and the results are promising. Achieving the highest storage capacity in MOFs recorded to date is a significant accomplishment.
- The metal incorporated materials have been prepared and characterized, and thus the project is tracking well. Unfortunately, the focus of the project seems to have been on determining gravimetric hydrogen densities rather than hydrogen binding energies, which should be the central focus of this project. The reviewer would have preferred a more quantitative answer from the principal investigator concerning the increase in hydrogen binding energy for the materials containing magnesium.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.5** for its collaboration and coordination.

- The measurement result of NU-100 should be independently validated in a timely fashion, as well as the porous polymer network material, PPN-4, from Texas.
- The reviewer considers validation of the results to be critical and feels results from validation testing should be provided if they have been obtained. The project needs to scale-up and obtain validation.
- The collaborations have improved.
- There have been limited collaborations, but the collaborations do include a quality partner for measurement validation.

Question 5: Proposed future work

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

- The future plan sounds good in general. It is not clear how the project will move from low coverage to high coverage for improved heats of adsorption.
- The project has effectively planned its future in a logical manner and has incorporated appropriate decision points. The collaboration is very likely to continue to be highly effective. Important new research and developments of existing excellent research are anticipated.

- The projected work seems worthwhile, but high heat of adsorption at high coverage seems like it may be very difficult.
- Predictive modeling work appears to be successful. More validation of the ability to predict new MOF structures should be pursued. Coordination of predictive modeling capabilities with other projects and internationally would be of benefit to the Program.
- It is nice to see that the measurement of enthalpies of hydrogen absorptions is planned for next year. The practical value of determining high-pressure, room temperature isotherms is unclear, as the crossover for any volumetric density advantage of porous materials over compressed gas is 200 atmospheres.

Project strengths:

- The project has good theory-guided bottom-up materials design.
- The work is of a high academic standard with publications of exceptional quality in *Nature Chemistry*, among others. The combination of researchers is internationally outstanding, and major advances in this area of physisorbed hydrogen storage are anticipated.
- The project has good theory and leverages previous work.
- Measurements indicate the discovery of a new MOF with very high hydrogen storage capacity (9 wt% excess capacity). Modeling of new MOFs has been shown to be successful at least in one case. The development and use of modified supercritical drying to synthesize MOFs that are unstable through standard processes is a big achievement.
- Strengths include the project team's outstanding synthetic expertise and ability to carry out high-quality, reliable material characterization and hydrogen absorption studies.

Project weaknesses:

- The measurement needs to be independently validated in a timely manner.
- There are no obvious weaknesses.
- The reviewer asks if the materials can be made at scalable levels. There needs to be external measurement validation.
- Given a record-breaking MOF capacity measurement, validation of the properties of this material should take a highest priority.
- The central premise of the project—that the presence of metal in MOFs will sufficiently raise hydrogen binding enthalpies to the point where room temperature stabilities can be achieved—lacks a firm fundamental basis.

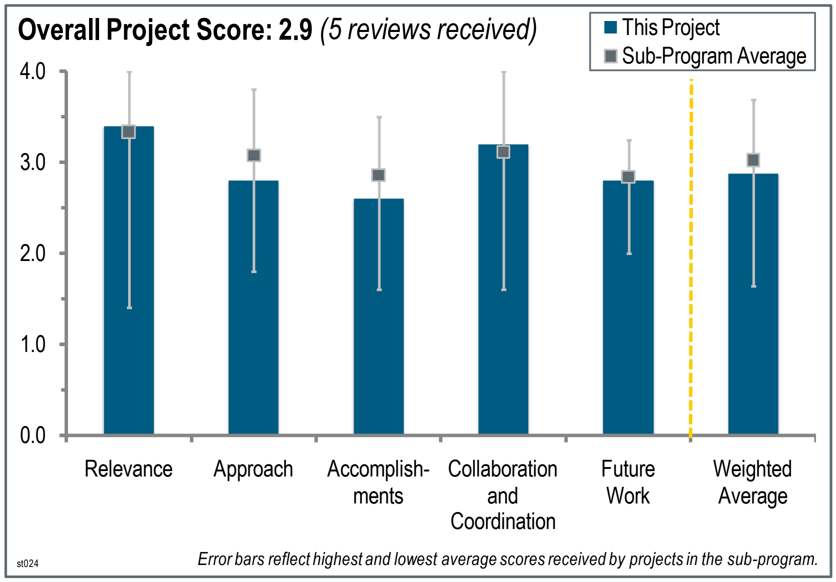
Recommendations for additions/deletions to project scope:

- This reviewer does not consider the progress to date to be commensurate with the project funding.
- Given a record-breaking MOF capacity measurement, validation of the properties of this material should take the highest priority. There has not been much progress made on POFs. Given the success in work on MOFs and the limited progress on POFs, this reviewer wonders if it would be appropriate to down-select between the two.

Project # ST-024: Hydrogen Trapping through Designer Hydrogen Spillover Molecules With Reversible Temperature and Pressure-Induced Switching

Angela Lueking; Pennsylvania State University

Brief Summary of Project:



The overarching objective is to synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable hydrogen spillover storage at 300–400 kelvin (K) and moderate pressures. In the past year, this project has: (1) focused on reproducibility studies and the effects of preparation conditions for one MMOF mixed with a platinum-carbon spillover catalyst; (2) improved the uptake and catalytic activity of the platinum/carbon spillover catalyst; (3) synthesized new MMOF structures and focused on the effect of oxygen functional groups; (4) increased the sensitivity and accuracy of volumetric measurements and compared single-sided to double-sided volumetric measurements; (5) reproduced literature on high-pressure uptake for platinum/carbon spillover materials at 80 bar and 298 K; (6) worked collaboratively with a Taiwanese institute to verify high and unique spillover results on a platinum/carbon-based sample; and (7) worked collaboratively to obtain in situ spectroscopic validation of spillover onto the carbon support.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to U.S. Department of Energy (DOE) objectives.

- The primary objective of this project at Pennsylvania State University (PSU) is to discover carbon materials where spillover processes from metal catalysts can give reversible hydrogen storage of several weight percent (wt%) at ambient temperature. If this capacity can be verified, spillover effects may give a pathway to materials that would approach the DOE targets for passenger vehicles.
- It is very important for us to understand the mechanism of spillover and its effect on room temperature hydrogen storage materials for automotive applications.
- This work is relevant to overall DOE objectives. Hydrogen trapping through designer hydrogen spillover molecules with reversible temperature and pressure-induced switching represents, if successful, is a major contribution to hydrogen storage research.
- The researchers are well aware of goals and needs for the DOE Hydrogen and Fuel Cells Program. The project milestones are very relevant to DOE goals.

Question 2: Approach to performing the work

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

- PSU has been investigating a series of carbon adsorption materials, mostly metal-organic framework (MOF) compounds with additives of microscopically dispersed platinum particles. This should allow the hydrogen spillover process to take place, thus giving significantly increased hydrogen storage capacities. PSU would continue studies to maximize storage capacities that are reproducible, as well as improve other properties such as the reaction kinetics.

- The synthesis reproducibility issues and the accuracy of volumetric measurements are the key issues for the Program to address. "Chahine's Rule" (1 wt% hydrogen adsorption per 500 square meters of surface area) is well validated for materials at cryo temperature. However, the principal investigator (PI) needs to validate if it is still true at 298 K based on published work from other groups.
- Great attention and consideration has been given to this experimentally difficult project. The project is very well designed with a good balance between experiment and analysis; the project is feasible and is integrated with other efforts.
- The project should not leverage work of Yang that has not been validated. It is good that the project is trying to show that results are reproducible. There is good awareness of kinetic issues for spillover. The project is not using the best techniques to probe the spillover mechanism.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- During the past year, PSU has revisited its techniques for measuring hydrogen capacities in order to improve accuracy and reproducibility. It has provided materials for others to measure and revisited past materials. It has decreased errors but did not verify past reports of room temperature capacities greater than about 1 wt%. The researchers have looked at various MOFs and means of adding the metal catalyst.
- When comparing the hydrogen storage materials with an empty tank, it is very important to also state at which pressure the comparison was done. One can easily draw the wrong conclusion from incomplete information.
- The project has achieved a number of very good accomplishments, but there is still a substantial degree of uncertainty regarding a considerable amount of the work. This is not because of a lack of capability of the project members (they are nationally recognized), but rather as a consequence of the difficulty of the subject matter.
- The project has excellent measurement capabilities and calibration as well as validation. Evidence for spillover is weak. Deviation from the Chahine Rule is not strong evidence for the spillover mechanism. Material development is limited to MOFs with spillover catalysts. The reviewer questions if this is the best system. Structural characterization of MOFs mixed with catalyst and bridges are, again, not evidence for spillover.

Question 4: Collaboration and coordination with other institutions

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

- PSU continues to collaborate closely with the co-PI at Rutgers University, who is synthesizing different MOFs with properties for potentially greater hydrogen capacities. PSU has also interacted with several other groups on characterizing samples and looking to verify reproducibility of the capacity measurements.
- The project has good collaborations between universities and laboratories.
- The collaboration is good and compact, but could perhaps be strengthened in terms of modeling and surface analysis.
- The PI collaborates well both externally and with co-PIs.

Question 5: Proposed future work

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

- The researchers' plans for preparing and characterizing modified MOFs and depositions of platinum metal are reasonable. This project has a critical go/no-go decision point of demonstrating 5.5 wt% hydrogen capacity at "moderate" temperatures by February 2012. Based on results obtained by the team to date, this goal is probably not achievable.
- The planned future work is good in general. Because there was only one spillover sample that showed an actual improved hydrogen uptake, there should be more focus on this sample to understand the mechanism of spillover.
- The project has effectively planned its future in a logical manner and has incorporated appropriate decision points. The collaboration is likely to continue to make progress, but should be very critically reviewed next year.

- The project seems to be on track for validating mechanisms. Looking at other materials for spillover could be valuable.

Project strengths:

- PSU undertook a committed effort to improve the accuracy of its methods for measuring storage capacities that included interactions with other organizations. The researchers have revisited issues of doping materials and looking for more promising candidates to be studied.
- Working on synthesis reproducibility issues and the accuracy of volumetric measurements can really help the Program draw meaningful conclusions.
- The project work is methodical and carefully undertaken.
- The project has very good measurement techniques. The accuracy is convincing and has been validated.

Project weaknesses:

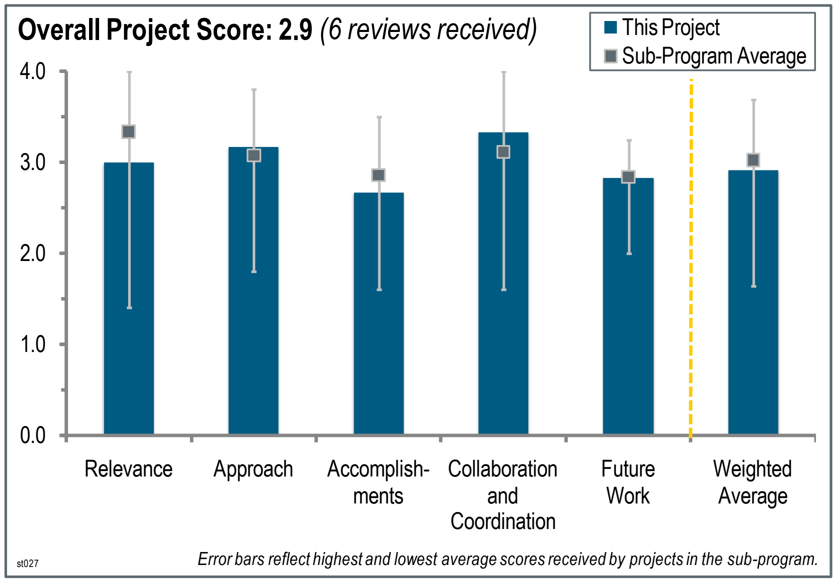
- Reproducible and accurate measurements of hydrogen storage capacities remain a major challenge with small samples. Apparently the processes and procedures both to prepare the MOFs and to incorporate the catalysts remain difficult and may still result in irreproducible measurements. Very slow kinetics for the transfer of hydrogen during the spillover process will still be a serious issue even if capacities are demonstrated to be greater.
- Other than reproducibility and accuracy, there should be more focus on the fundamental understanding of the mechanism of spillover to determine the limitation of this improvement.
- Spillover is a very difficult subject in which to derive accurate data and information. The project has made important methodological developments, but there are still substantial concerns about interpretation and reproducibility (see slide 23 of the 2011 presentation). There are also concerns about the data analysis (slide 41), which indicate something likely to be as trivial as a truncation of data precision in a data file.
- The project needs spectroscopic, nuclear magnetic resonance, neutrons, etc., to validate mechanisms. Deviation from the Chahine Rule does not prove spillover.

Recommendations for additions/deletions to project scope:

- The PSU-Rutgers team should strive for reproducibility in sample preparation (especially during dispersion of the catalyst) and attempt to produce larger amounts of materials to decrease sources of error and variations in the capacity measurements. Furthermore, the team should interact and contribute as much as possible with National Renewable Energy Laboratory's ongoing Weak Chemisorption project.
- No additions or deletions to project scope are recommended, but there will be careful consideration next year.
- Perhaps the project should have more focus on materials other than MOFs.

Project # ST-027: Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis Using Ordered Polymer Templates

Mark Allendorf; Sandia National 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 2011 are to: (1) demonstrate the effect of size on complex hydride thermodynamics, including sodium aluminum hydride ($NaAlH_4$) in metal-organic framework (MOF) templates, lithium borohydride ($LiBH_4$) in block copolymer templates, magnesium hydride (MgH_2), lithium amide, the quaternary hydride, and calcium borohydride; (2) demonstrate compositional tuning effects by predicting the magnesium-aluminum-hydrogen phase diagram and infiltrating templates and measuring hydrogen desorption; and (3) complete and submit journal articles.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.0** for its relevance to U.S. Department of Energy (DOE) objectives.

- The main goal of the project is to achieve tunable thermodynamics for hydrogen storage materials by controlling nanoparticle size. The control is achieved by confining the storage material into nanosize pores of 10–200 Angstrom of different materials (MOFs, covalent-organic frameworks, zeolitic imidazolate frameworks, and block copolymers). It is one of the approaches that explores ways to bring thermodynamics and kinetics of a storage material to the engineering requirements. The approach certainly makes the criteria of cost very difficult to fulfill.
- The project has excellent fundamental science, but the materials that will never be useful for hydrogen storage. However, there is a need to determine if nanotechnology has any use in storage.
- Nanoconfinement is a potentially powerful way to favorably alter the thermodynamics and kinetics of hydrogen sorption reactions in simple and complex metal hydrides. The systematic study of nanoconfinement effects on sorption reaction thermodynamics and reaction rates being conducted in this project can provide information that may be vital to understanding how to tailor nanoscale-directing structures to optimize hydrogen storage capacity and sorption characteristics. The project is directly relevant to the DOE Hydrogen and Fuel Cells Program goals and research, development, and demonstration objectives, especially in the area of improved metal hydride materials.
- The project is clearly relevant to DOE objectives.
- Nanoencapsulation appears to be the only approach for making complex hydrides viable storage materials.
- The project goal of reducing the metal hydride desorption temperature is an important goal for the Program objectives.

Question 2: Approach to performing the work

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

- It is a well designed project with four major directions: (1) synthesis of a wide range of materials that cover pore sizes from micro- to meso-scale; (2) delivery (infiltration) of different hydrides of interest to the pores; (3) characterization of structures and desorption; and (4) theoretical insight (Quantum Monte Carlo, density functional theory). The approach is integrated, and it is feasible to synthesize the desired material. The reviewer doubts if the desired thermodynamic, kinetic, and gravimetric properties of interest to the automotive industry will be obtained through this approach. Besides the difficulty of altering bulk properties, the design significantly reduces the overall gravimetric capacity compared to bulk. If less than 50% of MgH_2 goes to pores, then even with the best property it will be comparable to some easy-to-manufacture intermetallic alloys.
- The approach is fine, but currently there are no materials identified that can meet DOE targets. Some indication of how targets can be met by this project is necessary.
- The approach focuses on using ordered framework structures with well defined pore sizes as confinement media for metal hydride reactants. The effect of scaffold pore size and surface structure on the thermodynamic and kinetic behavior of metal hydrides is being studied systematically for the first time. The approach is innovative and well designed. There are clearly risks associated with unwanted reactions between the metal hydride and the template, as well as with incomplete incorporation and poor retention of reactants in host framework(s). These potential challenges are addressed in part through the use of different scaffold structures and by using different methods to incorporate the metal hydride reactants. In addition, a variety of analytical tools (including a novel modulated beam mass spectrometric technique) is being employed to identify gas-phase species and solid-state reactants and products in the host matrix. A companion task on theory and modeling directly complements the experimental effort (especially in the areas of compositional tuning of thermodynamics and nanocluster stability). That task is providing useful information to guide future experimental work.
- It is shown that in some cases nanoconfinement has a significant effect on thermodynamics and kinetics, and in some cases the effects are less pronounced.
- The general idea of decreasing particle size to reduce the stability of metal hydrides is not necessarily new. It is not apparent whether the approach will reduce the enthalpy value enough to meet the goals.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.7** for its accomplishments and progress.

- The project is progressing nicely. A large variety of nanoporous materials was developed, and infiltration of hydrides appears to work, e.g., for $LiBH_4$ and lithium aluminum hydride. There is a detailed study of $LiBH_4$ that demonstrated lowering the temperature of decomposition for 2–4 nanometer sizes and improved kinetics. Nice results were obtained for $NaAlH_4$, with a strong effect on kinetics and one-step transformation. Theoretical calculations give insight into energetics of small clusters and a threshold of bulk-to-nano behavior. Interesting progress was made for new magnesium-aluminum-hydrogen nanoclusters. Much more work is needed to evaluate the amount of materials in pores, its distribution, dispersion, etc. (the pressure-composition isotherm measurements suggest a very small percentage).
- Because these materials cannot make DOE targets, this reviewer asks what the next steps are, even if nanoconfinement works.
- There was good progress made in 2010 and 2011, especially in understanding size-dependent thermodynamic effects in nanoconfined $NaAlH_4$. Results for nanoconfined $LiBH_4$ were less definitive, presumably because of changes in reactant morphology and composition in the pores during heating. A significant difference in the reaction pathway is observed for hydrogen desorption from nano-confined $NaAlH_4$ compared to desorption from bulk $NaAlH_4$. The conclusion that nanoconfined $NaAlH_4$ decomposes via a one-step mechanism with a low activation barrier (versus a two-step process in bulk) is especially intriguing and provocative, and that result could potentially lead to enhanced hydrogen desorption at reduced temperatures in the nanoconfined material. A new direction for research on sorption behavior of MgH_2 that can be favorably tuned in mixed magnesium-aluminum-hydrogen nanoclusters emerged from the theory work. This has important implications for increasing hydrogen desorption rates at decreased temperatures.
- The project is making good progress toward the stated goals.

- Work on size-dependent thermodynamic effects of $NaAlH_4$ is very interesting and useful. The reviewer would like to have seen more progress on a broader range of systems having varying pore size or other high-capacity hydrides.
- The project has demonstrated some progress for the nanoconfined $NaAlH_4$, but it does not appear to provide thermodynamic improvement for other metal hydrides (i.e., $LiBH_4$). The practical implementation of this concept needs further progress to confirm the containablity of the nanoparticles in the pore structure.

Question 4: Collaboration and coordination with other institutions

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

- The project has good interaction and collaborations on both experimental and theoretical efforts with a number of institutions, including the National Institute of Standards and Technology (NIST); Sandia National Laboratories; University of Missouri, St. Louis; Massachusetts Institute of Technology; University of Illinois at Urbana, Champaign (UIUC); and Ruhr University in Germany. From the report it was not clear what the contribution was this year from NIST and UIUC.
- The research and development (R&D) team comprises experimentalists and theorists who have extensive experience and expertise in nanostructure theory and simulation of the properties of nanotemplates and clusters and complex hydrides. Solid collaborations have been established with UIUC (I. Roberston) on transmission electron microscopy analysis of nanostructures and Ruhr University on infiltration of hydrides in MOFs. The core team and collaborators are well suited to conduct the challenging experiments that the theory and simulation work demanded in this project.
- The project collaborations are satisfactory.
- The level of collaboration of the project is appropriate for this project.

Question 5: Proposed future work

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

- The proposed future work to modulate the thermodynamics of simple hydrides through compositional tuning and separate effects of size and pore chemical environment looks to be a logical extension with opportunities to discover interesting new materials.
- The project is ending, and further work should focus on high-weight percentage materials.
- Future plans represent a logical follow-on of the work conducted to date. A good combination of theory and modeling and experimental work is proposed. However, a candid assessment of technical obstacles and challenges has not been provided. Without that information, it is difficult to assess whether the future work is appropriate and whether the priorities are reasonable. A clear statement of technical risks and a detailed strategy for mitigating those risks (or overcoming technical hurdles) are needed. The project is nearly complete (86%). The future plans include far more work than can be accomplished during the remainder of the project. A thoughtful prioritization of future work is needed.
- The project reasonably builds on previous research.
- Additional work should be completed to confirm the theory about the reasons for the enthalpy and reaction path changes.

Project strengths:

- The project shows clear strength in its ability to deliver the proposed objectives, namely to synthesize materials with distributed nanoparticles of hydrogen storage material, and to control the sizes and improve property. At the same time, the experimental part has strong support and leads from theory.
- A well designed, innovative approach is being utilized to address an important R&D problem. The project has depth and scope sufficient to generate important results and conclusions concerning the thermodynamic and kinetic behavior of hydrogen sorption in nanoconfined simple and complex hydrides. The project team is extremely capable and the project is well coordinated and managed.
- A project strength is the exploration of the effects of nanoconfinement. There are good interactions between theory and experiment.

- This project is a valuable approach to improving the viability of a complex hydride.

Project weaknesses:

- The reviewer believes that there are two conceptual weaknesses of the project: (1) significant alternation of major bulk property, the enthalpy, is not achievable for most materials with reasonable dimensions; (2) dispersion of a storage material in pores significantly reduces overall gravimetric density of hydrogen, thus making the material impractical. Experimentally, much more work is needed to evaluate the amount of materials in pores, its distribution, dispersion, etc. (the PCI measurements suggest a very small percentage).
- In most of the systems studied thus far, it has been difficult to unambiguously distinguish between thermodynamic and kinetic effects. Also, possible reactions between the template and the metal hydride have not been unambiguously identified (or ruled out). Those reactions will undoubtedly have important ramifications in the interpretation of the results and the understanding of reaction mechanisms.

Recommendations for additions/deletions to project scope:

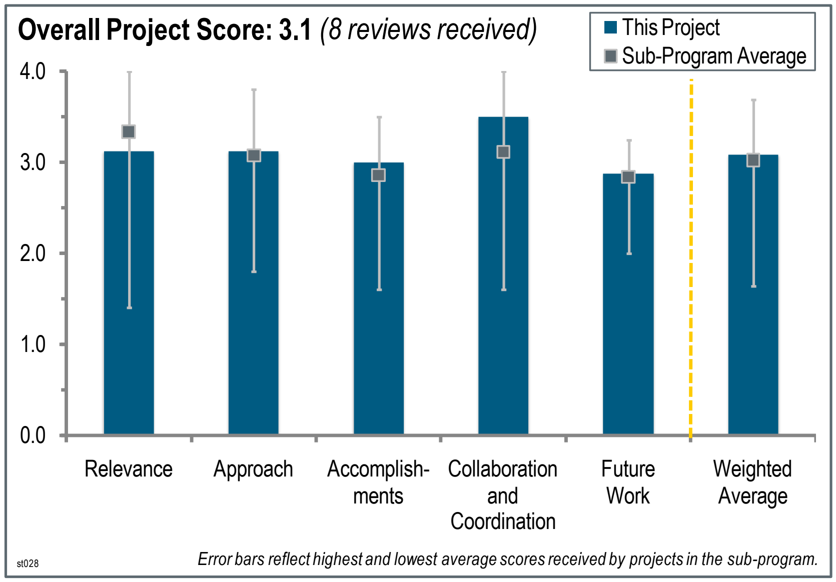
- It would be helpful if the results on $NaAlH_4$ and $LiBH_4$ could be compared with results obtained in related nanoconfinement studies (e.g., work from Max Planck Institute, HRL Laboratories, United Technologies Research Center), so that the kinetic and thermodynamic changes observed here could be put into a broader context (e.g., if there are systematic differences in properties apparent in different scaffold types, pore sizes, or infiltration methods). Also discrimination between thermodynamic and kinetic effects in scaffolds with different pore sizes and types should be an important focus of the future work.
- The work should continue as planned.

Project # ST-028: 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 the U.S. Department of Energy's (DOE) Centers of Excellence. 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., lithium amide ($LiNH_2$) and ammonia borane [NH_3BH_3]) and novel multicomponent complex hydride materials and reactions.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.1** for its relevance to DOE objectives.

- The project has a strong relevance to DOE Hydrogen and Fuel Cells Program goals.
- This joint project of Northwestern University (NWU); University of California, Los Angeles (UCLA); and Ford involves the prediction and demonstration of mixed component (i.e., sodium, magnesiuum, boron, and nitirogen) hydrides with large storage capacities such that DOE targets for passenger vehicles might be met. Experiments are being used to determine as-prepared and decomposition phases in order to ascertain reaction pathways. The team is also looking at catalysts to enhance the kinetics (apparently, only for desorption so far) and theoretically identify the mechanisms that control the kinetics. The team's objectives generally comply with DOE targets and goals.
- For the most part, the focus of the proposed work is to study metal hydrides. The chemical hydride ammonium dodecaborate $(NH_4)_2(B_{12}H_{12})$ is also being studied, as well as the salts of $B_{12}H_{12}$ with other cations such as the lithium ion. There do not seem to be any novel materials here. This project is a follow-on to the work of others. The work is in line with DOE objectives, but it is hard to determine its complete relevance to them from the slide package submitted for review, as well as because the team lead was not available for the presentation. This reviewer did not consider the presentation to be comprehensive or strong. The experimental focus is on mixtures of magnesium borohydride ($Mg[BH_4]_2$) and lithium borohydride ($LiBH_4$) as well as on the analogous amides.
- The goal is hydrogen storage materials discovery. The barriers addressed are gravimetric and volumetric storage targets and storage system charge and discharge rates. In principle, this project should support Program goals and objectives. The best measure of whether or not it does support Program goals will be determined by how close the project comes to achieving truly "relevant" results in the coming years.
- The project addresses three objectives: a lack of understanding of hydrogen physisorption and chemisorption, system weight and volume, and charging and discharging rates.
- The use of theory and experiment in the search for viable storage materials is a good use of Program resources.
- The search for new hydrogen storage materials is highly relevant.
- The project is relevant to some of the DOE automotive-based targets and objectives, in particular weight, rate (kinetics), temperatures, and reversibility. The project is not oriented very well to some DOE targets (e.g., volume, gas purity, cost, and energy efficiency). (During the question and answer session, the presenter responded that the volumetric hydrogen-densities for all of the materials studied were good).

Question 2: Approach to performing the work

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

- There is a good combination of theory and experiments to screen for new material combinations from distinct categories. There are many different aspects to the work: materials discovery, catalysis, thermodynamics of nano materials, kinetics, and diffusion. However, the group may need to further focus the research. It is an outstanding research team and expectations should be high. The reviewer asks how accurate the calculations on amorphous materials such as the "AlB_4H_{11}" material are. The reviewer wonders if the two aluminum environments predicted by Nuclear Magnetic Resonance are in error. The calculations appear to suggest only one aluminum environment.
- The approach to discover improved hydrogen storage materials is a combination of state-of-the-art first-principles calculations (NWU and UCLA) of possible hydrides and their reactions. Conventional volumetric measurements of storage capacities and kinetics are performed at Ford and NWU. The NWU researchers are also looking for more effective catalysts. While these materials are characterized by X-ray diffraction and infrared spectroscopy, other techniques (e.g., Nuclear Magnetic Resonance [NMR], and Raman and neutron scattering) would be very useful to identify reactants and products more completely, especially because many systems are amorphous and/or highly disordered.
- The approach is a combined computational and experimental effort. The team has made the materials and is characterizing them and their ability to release hydrogen.The researchers are adding cobalt on activated carbon and titanium trichloride in some cases as well. The reviewer asks how the researchers know what the products are. The reviewer also asks whether the researchers are making a metal boride and if the material can be recycled. There is little work being done to study the spent fuel. The focus of the computational work is on the prediction of new materials in the solid state. An issue is that there is no computational work on the release mechanisms or the kinetics. Of course, with the methods in use, the team probably cannot do this, as it does not have the tools in place to do the chemical searching nor find transition states reliably. There is no computational work in support of the "catalyst" development.
- The approach used in this project combines theory and modeling and experiments an with automotive industry perspective. The presentation at the 2011 Annual Merit Review did not leave a strong impression that all of the connections were working as effectively as one would hope.
- The approach to performing the project is effective and may bring good results in overcoming addressed barriers.
- The theoretical screening to narrow the synthetic search constitutes a best practice for exploring these materials. If the Program is aimed at onboard reversible materials, the project should have some component to look at hydrogenation as well as dehydrogenation.
- The combination of computational predictions, materials synthesis, and hydrogen storage measurements is excellent.
- The project is an excellent combination of a priori computation, experimental measurements, catalyst development, automotive needs, and engineering perspectives. This is one of very few projects looking at the important area of reaction paths from a calculational perspective.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- Improving the understanding of hydrogen physisorption and chemisorption is an especially worthy goal, but it may be too broad to quantify with current resources. The reviewer assumes it is related to the catalysis work using metals on carbon supports to activate hydrogen. The catalysis work may be the least developed to date, and it is difficult to understand the goal of developing a catalyst that can be used for everything. This goal may not be realistic, but it is used as a weak rationale for studying sodium aluminum hydride ($NaAlH_4$) decomposition. It was not clear if the reversibility of $NaAlH_4$ was investigated. If not, it is not worth the resources, unless the group can provide a strong scientific rationale for why a catalyst that works for $NaAlH_4$ would be expected to work for borohydrides or mixed material categories. The dehydrogenated products are not similar, and the reviewer wonders if the same catalyst should work for regenerating $NaAlH_4$ from aluminum and borohydrides from $B_{12}H_{12}$.

- Some potentially attractive candidate reactions have been theoretically predicted and at least partially verified by testing, but none appear to have the highly desirable reversibility behavior at moderate conditions. The use of 30 weight percent (wt%) of an additive or catalyst to lower hydrogen desorption temperatures of $NaAlH_4$ and a mixed magnesium-boron nitrogen hydride mixture may have some promise, although it significantly impacts storage capacity. Furthermore, the modest reduction-ammonia generation for the latter material shown on slide 15 of the presentation is very far from meeting purity expectations for fuel-cell-powered devices.
- There seems to be a lack of focus of the team on appropriate targets. Computational effort to support the catalysis effort is lacking. There is no computational work to support the development of an understanding of the mechanism. The group has performed significant work in collaboration with Dr. Zhao at Ohio State University on a project that is nearing completion.
- The experimental work seems to be quite good, but there could be improved coordination between the various teams. It seems that Ford is driving the experimental testing and that Dr. Kung at NWU is doing the catalyst development. It would have been helpful to see how the team is really interacting and how the catalyst and materials characterization teams are coordinating their efforts. The mass transport model is nice, but the reviewer is surprised that there are no chemical barriers. The talk suggested that the reaction barriers are due to mass transport, which does not fit with what the reviewer knows of the chemistry of these species. This may be due to this reviewer's misunderstanding. However, if the processes are mass transport dominated or limited, then there is no need to develop catalysts except for catalyzing the diffusion of the vacancies. This is not what the cobalt catalyst is doing and does not fit with the researchers' model of how the catalyst operates. The software methods development for prototype electrostatic ground state (PEGS) is interesting but seems to be more related to basic energy science rather than a need for the current work. The reviewer asks if the members of the team are now arguing that the hydrogen release is being driven by nanoparticles. If so, then they do not really need PEGS or even density functional theory to do this. Instead, the research team needs to use accurate molecular orbital based methods, with which the team has no experience. The reviewer asks what the connection is between the nanoparticle work and any experimental work.
- Predicting new compounds and then proving they can be synthesized is interesting, but if the new compounds do not meet one or more of the DOE targets, nothing of consequence will be accomplished. The summary of technical accomplishments given at the end of the presentation reported synthesis and characterization as well as prediction, extension, and development with no resounding findings that show meeting of DOE targets or the overcoming of barriers. The reviewer did not feel that the comparisons of experiment and theory were significant, especially for cases such as the phonon density of states versus neutron spectra comparisons.
- According to the co-principal investigator (co-PI), the project is 40% complete (compared to 50% of the funding time period). Synthesis and characterization (X-ray diffraction, infrared [IR], temperature-programmed desorption) of two predicted hydride mixtures, $5LiBH_4 + 2Mg(BH_4)_2$ and $Mg(BH_4)_2$ + magnesium amide ($Mg[NH_2]_2$), are completed. A new metal-carbon catalyst is tested on $NaAlH_4$, and applied to $Mg(BH_4)_2 + Mg(NH_2)_2$.
- The project has made good progress in both theoretical and experimental areas. Materials do not appear to meet Program goals. Theoretical identification and prediction of stable decomposition products is a significant development. Use of a supported cobalt catalyst is a significant discovery.
- The project has very interesting new catalyst results. Desorption temperatures of the materials being studied are still on the high side. Catalyst work is targeted at reducing these temperatures. The reviewer asks what are the reversibilities of the materials being studied, and what are the issues associated with ammonia or diborane evolution from the materials being studied.
- There has been generally very good progress on all four fronts of the work plan. There are a number of different mixed materials being investigated simultaneously. It is not completely clear which ones are the most promising and deserve the most future focus.

Question 4: Collaboration and coordination with other institutions

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

- The project has a strong team with excellent external collaborators.
- Excellent interaction and collaboration is indicated for this team as well as with other organizations.

- The team has good collaborations internally and externally. However, there is a lack of focus and a lack of project coordination by the PI. The individual efforts are doing good work, but there is no coordination or focus on a set of materials. The team is mixing known hydrides. The catalyst work is not coordinated with the materials characterization work, so one does not know if the catalyst is really a catalyst. No evidence was given that the starting material was regenerated with an intact catalyst. The computational work is not focused on mechanism or catalyst development. Rather, the PI is doing computational work in support of other efforts not relevant to the core work of the effort.
- Collaborations within and outside the project seem effective. The three principal partnering institutions appear to be equally engaged in the work of the project. However, in the question period following the AMR presentation, the presenter from UCLA and a team member from Ford were not able to give authoritative answers to questions concerning some aspects of the work being done at Northwestern.
- Unfortunately the co-PI did not reflect the full degree of collaboration within the project team and could not answer the questions beyond his responsibility area.
- Although only two organizations are officially participating, several outside entities are involved. Coordination between experimentalists and theorists appears to be working well.
- The project has an excellent set of collaborations.
- The collaborations are excellent and seem to be working well.

Question 5: Proposed future work

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

- The reviewer is very concerned about the catalysis effort. The catalysis project lead is very reputable, but the work described is not up to expectations. The cartoon provided for the catalysis approach suggests hydrogen spillover. The reviewer wonders if there is some precedent that “spilled-over hydrogen” would reform a complex hydride from aluminum. The reviewer asks about the reverse reaction—if there is some rationale to suggest that the hydrogen comes off of the complex hydride onto the carbon and needs a metal to recombine. The theory work is being used to study the decomposition mechanisms of the materials. If the mechanism is understood, the reviewer wants to know if this could be used to select appropriate catalysts that would optimize the decomposition reactions.
- Experimental verification of proposed reactions of $(NH_4)_2B_{12}H_{16}$ and the magnesium-boron-nitrogen hydride phases should be performed. Also, extending and expanding the first-principles calculation of the kinetics for mass transportation should be very productive because the intrinsic kinetics appear to rate limiting for reactions of the aluminum hydrides and borohydrides.
- The reviewer does not see the purpose of the $B_{12}H_{12}/(NH_4)_2$ work. $B_{12}H_{12}$ is a sink and the production of boron nitrides will not be good. The computational work should focus on mechanism development and catalyst development. If diffusion and mass transport are important, catalyst development is irrelevant. There does not seem to be any reason to go after the prediction of new materials computationally unless the direction of the experimental part of the team is going to change direction as well. There is no synergy between the experimental and computational efforts.
- The proposed future work looks like a continuation of the prior work. Analysis of hydrogen storage systems for different storage media and concepts is showing that the weight percent (wt%) hydrogen in the storage material itself will have to be at least twice the 2015 system target. That being the case, the only materials that should be addressed by this project are ones that can store and deliver 11–12 wt% hydrogen. Anything less than that is not worth working on. The notion that a project such as this one should seek new understanding of hydrogen storage and release phenomena is a noble one, but there is not enough time left for that kind of thinking. The Hydrogen Storage Engineering Center of Excellence needs results that it can use now.
- The plans are built on past progress and generally address overcoming claimed barriers.
- There is no work proposed on the reverse reaction.
- The future work activities are very well structured.
- The project is reasonable, but a little on the broad side. More focus and specifics might have been justified.

Project strengths:

- Top-flight groups that have developed very insightful and effective computation procedures are performing the theoretical studies. A strong working relationship has been established between the academic and industrial partners that facilitates productivity in this project.
- Individual team members have good strengths and are very accomplished scientists. They have good computational and experimental tools and capabilities for some of the work, but not all aspects.
- This project has good scientists working on it who are coming up with some new directions for materials discovery and material performance improvement.
- There is a strong fundamental basis of research in the project that could allow for successful implementation.
- The project effectively integrates the expertise of several strong investigators to achieve results.
- The project has an excellent approach, team, and collaborations.
- The project has a useful combination of computation, experimental measurements, catalyst development, and automotive perspectives.

Project weaknesses:

- Only hydrogen desorption behavior was described from the experimental studies, while reversibility is highly desired. The large amount of additives needed to improve desorption kinetics is a problem and a scheme to create a more fundamental approach is lacking. Using primarily X-rays and IR to characterize these materials is insufficient, as often the most interesting species are amorphous.
- There is a lack of coordination in the project by the PI, and a lack of focus on a specific set of problems. There is no mechanism development or computational modeling of intermediates and kinetics except for diffusion and defects. There is a critical issue of whether catalysis is relevant if diffusion or defect motion is the slow step. There is a lack of data in the submission of review material. There is no publication or presentation list. There was no response to reviewers' issues from previous years. The project lacks go/no-go decision points. The project is lacking in planning for future work.
- The reviewer took exception to the emphasis on the catalysis results based on adding 30% extra mass in the form of co-doped carbon. That extra mass should have been included in the calculations of the wt% hydrogen release estimates.
- There was a lack of information in the presentation about previous reviewers' comments and the team's response to them.The list of proposed promising mixtures is short.
- The issue of simple and efficient materials synthesis needs to be addressed at some point. Unless the final products can be simply regenerated to form the starting materials, the materials will not be practical.
- Perhaps a little more attention is needed on reversibility and reaction by-products.
- The project does not address some of the important DOE objectives and targets: cost, impurities, etc.

Recommendations for additions/deletions to project scope:

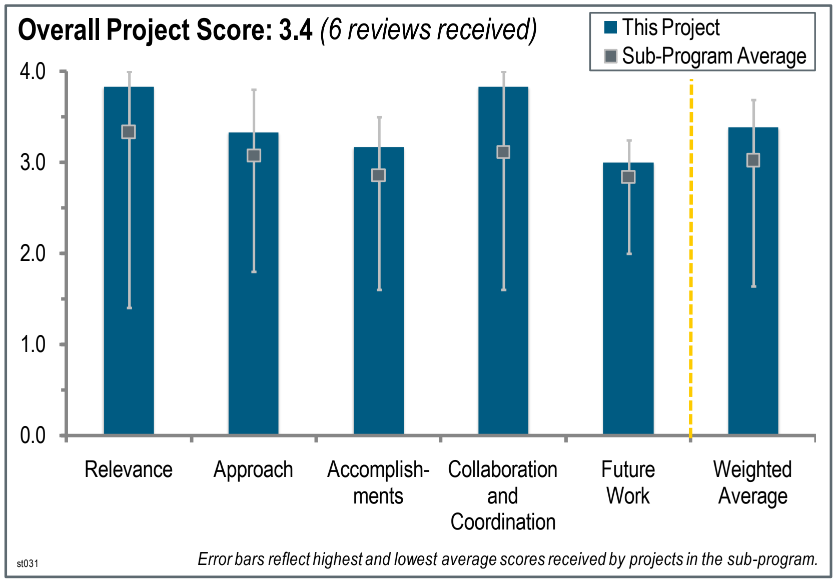
- The reviewer would recommend that additional techniques such as NMR and neutron scattering be used to characterize any promising materials and their reaction products. To have a more complete vision of the catalyst/additive, phases that allow both absorption and desorption should be investigated along with reducing the amount of these additives.
- There should be a focus on mechanism development and the question of whether a catalyst is needed. If diffusion, defects, and vacancies are critical, as suggested by modeling, the team should eliminate the catalysis effort. If catalysis is important, then the researchers should determine why modeling results are incorrect in determining the rate-determining step. There is a lack of consistency. It is unclear to this reviewer whether the catalyst is a catalyst, or if it has changed the material in terms of becoming a new product. The project needs to focus the computational effort on supporting the overall project. It is currently too diffuse in support of other efforts. The project leader should attend the review. A full set of review materials should be provided in the future.
- It would be desirable to extend the list of proposed promising mixtures.
- Consider working on regeneration of dehydrogenation products to reform hydrogenated starting materials.
- Show the volumetric hydrogen capacities in future presentations and reports.

Project # ST-031: 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 have the potential to meet the U.S. Department of Energy's (DOE) kinetic and system gravimetric storage capacity targets. Current investigations include: (1) reversible dehydrogenation of magnesium borohydride ($MgBH_4$) (14 weight percent [wt%] theoretical, greater than 12 wt% demonstrated reversible capacity); (2) lithium scandium borohydride ($LiSc[BH_4]_4$) (14.7 wt%); (3) sodium scandium borohydride ($NaSc[BH_4]_4$) (12.8 wt%); (4) and sodium manganese borohydride (6.9 wt%) in the 100°–220°C temperature range.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.8** for its relevance to DOE objectives.

- Finding a high-capacity (greater than 10 wt%) reversible metal hydride is essential for vehicular hydrogen storage. The favorable thermodynamics and kinetics are also very important to the DOE Hydrogen and Fuel Cells Program.
- The relevance of this almost-concluded project to the overall DOE objectives is evident.
- There are currently no metal hydrides that meet the DOE's goals for gravimetric and volumetric capacity and operating temperature. Consequently there has been an intensive search for compounds that can cycle hydrogen reversibly at temperatures and pressures commensurate with fuel cell operation. This project focuses on a promising class of reversible, high-capacity borohydride compounds that can potentially cycle under mild conditions. The project is closely aligned with the Program and DOE research, development, and demonstration objectives.
- The project is concerned with very high-capacity hydrides.
- Investigation of magnesium borohydride $Mg(BH_4)_2$ and ionic complexes can directly impact the Program because both groups of materials have the potential for reversible hydrogen storage.
- This project is focused on practical aspects and the critical challenges for complex hydrides. It has a strong capable contributor in the complex hydride hydrogen storage materials class.

Question 2: Approach to performing the work

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

- Nano-confinement and re-hydrogenation in non-conventional solvents are effective approaches.
- The project was focused on four of the critical barriers, namely system weight and volume, charging and discharging rates, thermal management, and the lack of understanding of hydrogen chemisorption and physisorption.
- The approach focuses on the characterization of a new class of borohydride complexes, $Mg(BH_4)_2$, and anionic transition metal borohydrides with a high capacity for hydrogen storage. In addition, new approaches for

nanoscale reactant confinement and new solvation approaches have been explored. The approach in 2011 focused primarily on characterizing sorption cycling in $Mg(BH_4)_2$ and evaluating the sorption properties of the anionic transition metal borohydrides. The approach is a direct and natural extension of the work conducted previously on the project. The approach is well formulated and is focused keenly on the critical technical barriers encountered by virtually all complex metal hydride systems, including high-capacity cycling of hydrogen under conditions of moderate temperature and pressure and at rates compatible with transportation applications.
- Work on the reaction of hydrogen with magnesium boride (MgB_2) is very good. Most anionic transition metal borohydrides contain scandium, which is impractical due to the high cost of scandium.
- Nanoconfinement of $Mg(BH_4)_2$ and adjustment of the ionic character of ionic complexes to improve hydrogen storage properties are good approaches with potential to overcome the barriers.
- The approach has several research thrusts with well defined scopes and tasks, and there is a great balance between achieving a detailed fundamental understanding of reactions and assessing high-level practical hydrogen storage properties.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The work on lowering the regeneration conditions of some of the materials has progressed nicely.
- The project is 98% complete, and the main goals have been achieved; the implementation of the project may be considered successful.
- Although the goal of reversible cycling at high capacity (greater than 10 wt%) under mild reaction conditions was not achieved in 2010–2011, the $Mg(BH_4)_2$ system exhibited the highest capacity for a reversible borohydride system to date. The compound exhibited multiple sorption cycles at very high capacity, cycling between $MgBH_4$ and MgB_2. However, the temperature was prohibitively high for fuel cell applications (530°C). Recognizing that hydrogen desorption from $Mg(BH_4)_2$ is a multi-step process, the principal investigator (PI) and his team conducted a systematic and informative follow-up study on the cycling between selected steps. Although cycling of lower capacity material was observed, the temperature was reduced by nearly 200°C. These are intriguing results that could provide a pathway to the discovery of new borohydride materials with improved performance. The hydrogen sorption characteristics of the anionic transition metal borohydrides were less promising. The hydrogen capacities were far lower than the predicted values, and cycling was problematic.
- This project is making good progress.
- Improvements have been achieved using nano-confined $Mg(BH_4)_2$; however, the hydriding and dehydriding temperatures remain high. The demonstration of the reversible partial dehydrogenation of ionic complexes is commendable, but still far below the DOE research and development targets.
- This project has made great progress on magnesium borohydride reversibility and focused on practical properties and practical property evaluation balanced with detailed characterization for improving fundamental understanding. The identification of intermediate borohydride phases capable of cycling under mild conditions is very useful toward circumventing thermodynamic and/or kinetic "traps." However, it appears that the most promising borohydride reversible phases revealed that they possess limited capacities (e.g., for $Mg[BH_4]_2$ to magnesium triborane). Hopefully these lessons can be extended to higher-capacity reactions.

Question 4: Collaboration and coordination with other institutions

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

- This project has good collaboration in terms of getting the material characterization work done.
- The team showed appropriate and well coordinated collaboration involving more than 15 institutions in the United States and abroad.
- Extensive and valuable collaborations have been the hallmark of the PI's involvement in the Hydrogen Storage sub-program. This project has been no exception. There are significant and important contributions from a large number of national and international collaborators in the areas of synthesis, material development, and characterization.
- This project has excellent collaborations.
- The collaboration with multiple teams is very impressive.

- The project leverages many significant collaborations in key areas that support the project's success, including nuclear magnetic resonance structure characterization.

Question 5: Proposed future work

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

- The future work is adequate.
- Despite project timing coming to an end, the future work represents a logical proposed extension of the current work and focus on continued progress on the critical barriers.
- The future work will add to the fundamental understanding; however, it is unlikely that it will lead to overcoming the barriers.
- The current dehydrogenation conditions for the listed borohydrides will not meet the targets for vehicular hydrogen storage applications.
- The proposed future work is limited to reaching the remaining aims, including the adjustment of conditions to maximize the trade-off between cycling capacity and temperature/pressures required for reversible dehydrogenation of $Mg(BH_4)_2$; determining if a material that undergoes reversible dehydrogenation under moderate conditions can be obtained from the initial dehydrogenation of $LiSc(BH_4)_4$ and/or $NaSc(BH_4)_4$ under mild conditions; and further evaluation of well-to-tank efficiency of the dimethyl ether/$LiAlH_4$ system.
- The technical work on the project has concluded, so a review of the future plans is not relevant. The submission of the final report remains as the final activity for this project.

Project strengths:

- This project definitely involves some interesting chemistry and the PI made positive progress toward improving the systems.
- This is an innovative research and development project conducted by recognized experts in metal hydride materials for hydrogen storage. The approach is well designed, and interesting results have been obtained that have led to improvements in the understanding of metal borohydrides for hydrogen storage applications.
- Extremely high hydrogen capacity materials are being considered in this project.
- This project is working on the critical materials that have the potential for a breakthrough in the Hydrogen Storage sub-program.
- This project has a strong, capable, and collaborative team with a strong balance of fundamental and practical barriers and understanding.

Project weaknesses:

- In order to meet DOE system-level targets, the PI needs to define what the material level is for the thermodynamics and kinetics target.
- The utility of scandium-based compounds for applications is unclear.
- Having only three focused areas is still too much for a project team.

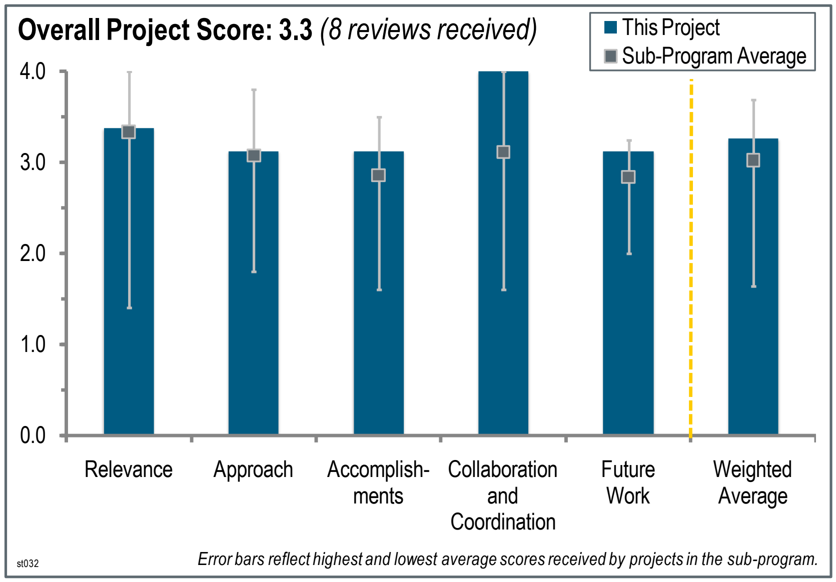
Recommendations for additions/deletions to project scope:

- Technical efforts on this project have concluded, so recommendations for changes in the project scope are not applicable.
- The project team should focus on only two critical areas.

Project # ST-032: 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 (greater than six weight percent [wt%]), lightweight hydride capable of meeting or exceeding the 2015 U.S. Department of Energy (DOE)/U.S. DRIVE targets. Objectives for fiscal year (FY) 2010 were to: (1) study the structure and hydrogen storage properties of two aluminum boranes—AlB_5H_{12} and AlB_6H_{13}—for hydrogen storage property measurements; and (2) synthesize and study other borane compounds. Objectives for FY 2011 are to: (1) complete the structure analysis for the aluminum borane AlB_4H_{11}; (2) perform a study on the absorption and desorption kinetics and catalytic effects to improve the reversibility of AlB_4H_{11}; and (3) complete a final report.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to DOE objectives.

- This project has good relevance to DOE's goals.
- This project has been sharply focused on the discovery and characterization of lightweight metal hydrides.
- New light materials with suitable thermo and kinetics are exactly what are needed to reach the goals and targets of the DOE Hydrogen and Fuel Cells Program. However, the project has drifted to spectral analysis and left the straight path of having high hydrogen cycling as the goal, otherwise this project would definitely have been given a rating of "four."
- This project has one notable feature; it truly focuses on the hydrogen storage materials that actually have at least a theoretical chance of meeting the 2015 gravimetric and volumetric system requirements. All of the materials the researchers study contain more than 10 wt% hydrogen, which is critical for meeting those 2015 system targets.
- This project aims for the main 2015 targets and the development of a high-capacity (greater than 6 wt%), lightweight hydride.
- This material has a high percent of hydrogen released; however, a high impurity level of diborane (B_2H_6) and a lack of reversibility hampers its utility.
- Studies of aluminoborane compounds such as AlB_4H_{11} can directly impact the Program, as this group of materials has the potential to meet the storage capacity requirement.

Question 2: Approach to performing the work

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

- The approach is very good and promising materials are selected/synthesized and studied in a comprehensive manner. Storage and decomposition mechanisms are also investigated.
- This project is well focused on the barriers, including right heat of formation (Barrier J), absorption/desorption kinetics (Barrier E), and reversibility for borohydrides (Barriers D and P).

- This project has done good work on synthesis and characterization and had good collaboration with theorists. The project needs to move quickly to addressing material reversibility.
- This approach has identified a number of interesting materials. Of late, the focus has been on the most promising material for reversible hydrogen storage, AlB_4H_{11}.
- The focus on structure characterization is reasonable, but parallel studies on catalysts to enhance the reversibility would be highly desirable.
- A new area of storage compounds is always welcome. This project is using the right tools to study this amorphous material. The reviewer, however, is concerned about the large effort of structurally characterizing the material, which does not seem to be able to be regenerated to any great degree. Hydrolysis (as in the B_3 materials discussed in this work) has been almost completely rejected as a method, so this is probably not a good focus.
- This project focuses on the experimental synthesis and characterization of novel borane structures.
- The central question for AlB_4H_{11} is whether it is reversible. An enormous effort was devoted over the past year to characterizing the structure of this material, but there appears to have been no effort devoted to reversibility.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- An incredible amount of good work has been performed to determine the structure of AlB_4H_{11}. The reviewer asks if there if the project can provide any insight into the structure of the product(s) to develop a strategy to increase reversibility.
- This high-capacity material is exciting, but only of it can be regenerated onboard. The per-cycle loss of B_2H_6 is significant (1.5% of starting material by the reviewer’s calculation), and must be reduced to near zero for viability.
- A great deal has been learned about AlB_4H_{11}, which may be very important for the future development of this material. The hydrolysis materials are interesting and they were indicated to be better than sodium borohydride ($NaBH_4$) and ammonia borane (AB).
- Identification of the structure of AlB_4H_{11} is significant; however, the hydrogen storage properties still need to be improved.
- The researchers seem to have pinned down the sub-structure of AlB_4H_{11} using a suite of techniques, but it is not completely clear whether they have the exact structure determined. The researchers made several other compounds and tested for suitability. So far they have not had any success, but they are doing the right work and understanding before moving on. The reviewer does not understand how calculated vibration structure of a crystal helps with determining an amorphous structure.
- Much detailed study has gone into elucidating the structure of AlB_4H_{11}, with only limited success. This is not surprising for a material that seems to be somewhat amorphous and somewhat polymeric. It is likely that the structure is complex, possibly discontinuous or irregular in nature, and beyond being fully resolved. What is more important in the context of understanding AlB_4H_{11} is the way it gives up and takes up hydrogen.
- The project is almost complete, with only minor sub-items to fulfill in the time left (the project is scheduled to end in August 2011).
- Little progress has been made on reversibility.

Question 4: Collaboration and coordination with other institutions

This project was rated **4.0** for its collaboration and coordination.

- This project has very good collaborations.
- This project’s collaborations are useful, diverse, and would be difficult to improve on other than in number.
- As slide six of the presentation shows, numerous institutions are involved in the characterization work, which seems well coordinated by the Ohio State University (OSU).
- The amount of work done in the past year is impressive for the funding level of $212,000. This reviewer wonders if it is possible that some of the results presented at the 2011 Annual Merit Review were achieved in the prior year. The presentation made it sound like all of the results were from work over the past year.
- The report shows a good coordination and close collaboration among all of the institutions involved in the project.

- This project has done good work with others to refine the structure.
- The project has had an excellent array of key collaborative efforts.
- Collaboration with multiple teams to identify the structure of AlB_4H_{11} is excellent.
- This project has several strong collaborations.

Question 5: Proposed future work

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

- The future work sounds reasonable, given the time left for the project.
- The reviewer asks whether partial reversibility just implies that different products are formed, and also wonders whether some are thermodynamically stable and others kinetically stable. If this is the case, the reviewer wants to know what the strategy for improving reversibility would be. Ammonium triborane has a greater solubility than AB, but the reviewer wonders about the solubility of the products after hydrogen release. The products must be very similar. The concern with the aqueous $NaBH_4$ approach was a change in phase. This resulted in a no-go decision. If the products are not more soluble, then it will be difficult to use these materials in applications.
- This project is focused on the things that matter. It could use a little more aggressive no-go strategy, but this reviewer understands that it is being performed in an academic setting and the principal investigator (PI) has pedagogical goals to achieve outside of those of the Program.
- The presentation of future work has little meaning for this project, which ends in August 2011. It looks like all there will be time and resources for is finishing up the story on AlB_4H_{11}.
- With only three months left until the end of the project term, only minor sub-items are planned to be accomplished, and they are clearly built on past progress.
- Work on reversibility was proposed, but no real information on the strategy for attaining reversibility was discussed.
- This project is 90% complete and ends in August 2011.
- It is unclear how solving the structure of AlB_4H_{11} will influence catalyst choice.

Project strengths:

- This project is working on a new material, has a strong PI, and employs an approach aimed at understanding to achieve function.
- This has been a well conceived and well orchestrated project. In terms of addressing materials with a credible chance of meeting hydrogen storage system targets, this project ranks among the best in the Hydrogen Storage Centers of Excellence projects over the past five years. The PI can take most of the credit for this. The leveraging of capabilities at other institutions was a key feature of the project and contributed to the successes achieved. The science was generally very good.
- This project has good characterization and synthesis.
- This project has excellent objectives, approaches, and results.
- The collaboration is excellent in this project.

Project weaknesses:

- This reviewer found no weakness in this project.
- The boron loss from B_2H_6 is not well approached.
- Some aspects of the data analysis, particularly experimental data and calculations done at other institutions, were not exploited to the fullest. Some of the spectroscopic results, the density of states calculations, and the neutron scattering data may have offered more in the way of discovery than the OSU team took time to cull from them.
- The lack of characterization of products after dehydrogenation is a weakness of this project.
- The screening of effective catalysts should be started earlier.

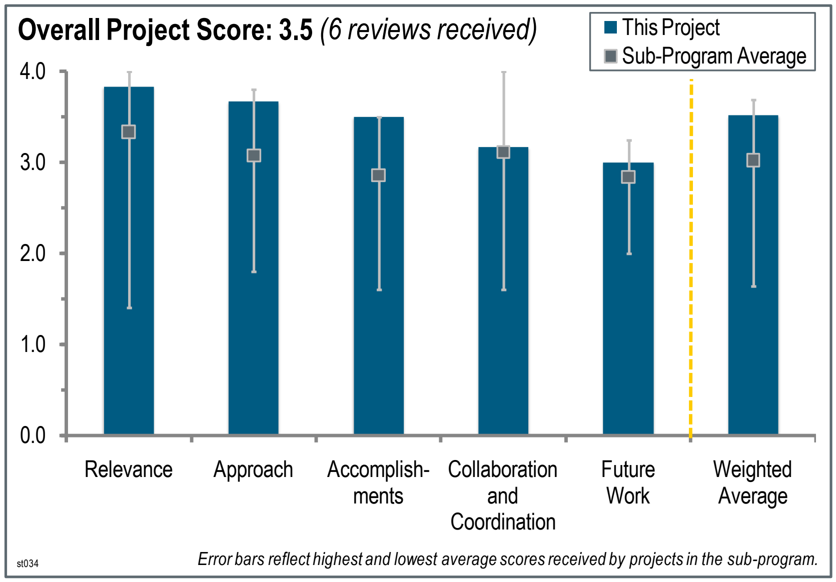
Recommendations for additions/deletions to project scope:

- If possible, the researchers should move to new materials sooner once it is clear that they are not going to work. If possible in an educational setting, the researcher should not tie-up every structural end or spectroscopic detail that is nice but not required. Either this group or some other group should be funded to work on B_2H_6 suppression. This project should stay away from hydrolysis, as it is not the aim of the Program.
- Their characterization efforts should be extended to include hydrogen-depleted material.

Project # ST-034: Aluminum Hydride

Jason Graetz; Brookhaven National Laboratory

Brief Summary of Project:



The overall objective of this project is to develop a low-energy pathway to regenerate aluminum hydride (also called alane) (AlH_3). The challenge is that AlH_3 is not onboard reversible. Objectives for this project are to: (1) meet the U.S. Department of Energy's (DOE's) technical performance targets using kinetically stabilized aluminum-based hydrides (e.g., lithium aluminum hydride ($LiAlH_4$) and AlH_3); (2) develop low-energy (fewer than 73 kilojoules/per mole of hydrogen or 30% of fuel energy) regeneration routes to prepare kinetically stabilized hydrides from the spent fuel; and (3) assist with the engineering design for an off-board system based on a kinetically stabilized hydride.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.8** for its relevance to DOE objectives.

- This project addresses virtually all of the DOE onboard storage system objectives in an unusually thorough manner.
- This project is strongly relevant to the DOE's hydrogen storage objectives. The project has revealed critical barriers and corresponding solutions in regard to AlH_3 as an onboard storage material.
- With a hydrogen density of 10.1 weight percent and 149 grams per liter plus the low operating temperature, this material is critical to support the DOE Hydrogen and Fuel Cells Program.
- AlH_3 is a critical material for hydrogen applications.
- The critical rate information on hydrogen release from AlH_3 is relevant.

Question 2: Approach to performing the work

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

- Experimental isothermal kinetic measurements are exactly what the engineering center needs for modeling AlH_3 for hydrogen storage systems.
- The slurry concept is a good approach to addressing the regeneration challenge.
- Even though "etherization" and "aminization" of AlH_3 adds a level of complexity in the regeneration of AlH_3, it is still a feasible approach because low hydrogen pressures can be utilized.
- AlH_3 is clearly one of the most promising alternatives for onboard vehicular hydrogen storage in terms of potential for meeting all DOE objectives. This project has some especially attractive approaches in the areas of AlH_3 synthesis, low-temperature catalyzed decomposition, slurry use, and systems considerations, among others. This is a very practical orientation.
- The approach to addressing ambient temperature stability (to circumvent a spontaneous reaction) through the fundamental understanding of reaction mechanisms and phases is appropriate for optimizing material and system design concepts.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- Impressive progress has been made on all fronts. The promise shown by catalyzed slurries is especially valuable and offers tank filling and dehydrided aluminum removal that will be roughly amenable to the current liquid tank filling infrastructure.
- The work on slurry approach and on catalyzed hydrogen desorption is promising.
- This is a great practical assessment of thermal cycling to ensure the hydrogen release is controllable and the induction period is reduced. The impact and optimization study of titanium-catalyst addition was well studied, along with a quantification of improvement. Such studies address the critical onboard barriers for AlH_3. The exploration of synthesis routes for controlled particle size, slurry characteristics, and scale-up are all highly relevant and targeted toward practical implementation of AlH_3 as a hydrogen storage material.
- This project has optimized the synthesis of micron-sized AlH_3 particles and the rates of hydrogen release from AlH_3 in slurries.
- With the slurry approach, the researchers are getting faster kinetics compared to dry AlH_3. This is a very interesting finding and represents great progress toward overcoming the barriers.
- This project is making reasonable progress toward the synthesis of AlH_3.

Question 4: Collaboration and coordination with other institutions

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

- This project has good collaborations.
- The collaborations are very good, at least on paper. Except for Argonne National Laboratory (ANL), the natures of the collaborations are not completely clear. The ANL collaboration on systems and regeneration (ST-001) is very valuable.
- This project complements and communicates with other AlH_3-based work, including with Savannah River National Laboratory (SRNL) and Sandia National Laboratories. Eventually—as the synthesis, onboard properties, and off-board regeneration properties are optimized—it will be useful to understand the well-to-wheels (WTW) efficiency (e.g., from ANL and/or the Hydrogen Storage Engineering Center of Excellence [HSECoE]) and industrial perspectives with respect to commercial synthesis. Thus, collaborations in those areas will become important.
- More pro-active communication with the HSECoE to make sure that AlH_3 is not forgotten as a potential off-board (chemical hydrogen storage) system is suggested.

Question 5: Proposed future work

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

- The future plans are excellent. It is time to forge a relationship with an industrial partner. AlH_3 can be a relatively near-term solution to the onboard storage challenge, and a potential large-scale domestic producer needs to be identified. AlH_3 is not a current item of commerce.
- The future work is a logical extension of current progress and focuses on the remaining practical and technical barriers. Transitioning information regarding optimized (catalyzed) slurries to the HSECoE and ANL for WTW and system evaluations (based on Brookhaven National Laboratory onboard and SRNL regeneration data) is encouraged.
- The proposed future work is good.
- The reviewer asks whether the faster observed rates in slurries are due to better heat transfer, and if it similarly explains the results that show removing the heat source from AlH_3 stops the reaction (there is no runaway reaction). The reviewer further asks whether the reaction slows down sufficiently when there is a slurry. Heat needs to be removed to stop the reaction, and this may be more difficult in an engineered system on a larger scale. This may need to be considered by the HSECoE. The reviewer also asks what the best solvent for slurry formation that can be removed for regeneration approaches is.
- Based on what the researchers learned, the plan is sufficient to address the challenges.

- This project needs to redouble the regeneration efforts. If slurries or catalyzed composites are used, the reviewer asks if this will complicate the regeneration process.

Project strengths:

- The approach is novel.
- AlH_3 is a promising material.
- This is a simple, powerful hydride technology and a very practical orientation.
- This is a highly capable team focused on critical practical and technical aspects of AlH_3-based hydrogen storage.

Project weaknesses:

- Rather than trial and error, it will speed up the progress if the principal investigator (PI) can incorporate some modeling work in predicting the research direction.
- The researchers need to find ways to simplify the synthesis process.
- Off-board regeneration is needed. This is certainly not a barrier, but similar to ammonia borane and sodium borohydride, this may create difficult challenges in terms of an effective cost of hydrogen.
- The researchers should strengthen the connection to the HSECoE for delivery of data and information, if not already underway.

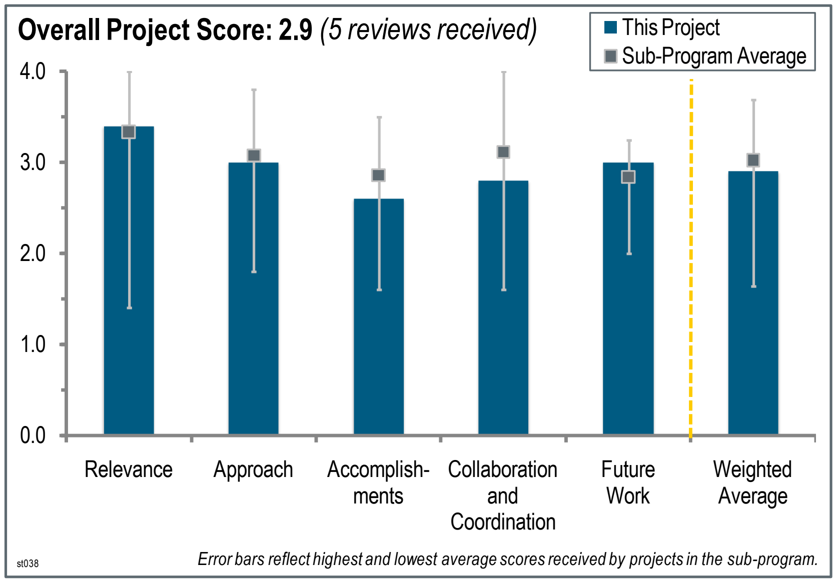
Recommendations for additions/deletions to project scope:

- The PI should further investigate why the slurry can improve the kinetics.
- The DOE's Office of Basic Energy Sciences (BES) has funded some of the PI's effort on AlH_3. Without knowing the details of what kind of research is supported by BES, this reviewer is concerned about duplication of effort under BES and DOE's Office of Energy Efficiency and Renewable Energy (EERE) funding. EERE management should verify that there is no duplication of effort.
- This reviewer had no recommendations except to explore an industrial partnership.

Project # ST-038: Hydrogen Storage by Novel CBN Heterocycle Materials

Shih-Yuan Liu; University of Oregon

Brief Summary of Project:



The overall objective of this project is to develop carbon-boron-nitrogen (CBN) heterocycles as novel hydrogen storage materials. The storage material criteria for this project include being in a liquid phase as well as having a gravimetric density of greater than 5.5 weight percent (wt%) (on a system basis), a volumetric density of greater than 40 grams of hydrogen per liter, (on a system basis), acceptable thermodynamics (hydrogen absorption and desorption), and spent fuel regeneration (reversibility). Objectives for this project are to: (1) synthesize novel carbon-boron-nitrogen heterocycle materials (first-fill synthesis); (2) provide a thermodynamic analysis of materials (experiment and theory); (3) formulate materials as liquids; (4) develop and identify conditions for hydrogen desorption (release) with the potential to meet U.S. Department of Energy (DOE) hydrogen storage targets; and (5) develop and identify conditions for regeneration from spent fuel.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to DOE objectives.

- Coupling exothermic hydrogen desorption from boron-nitrogen components of the heterocyclic system with endothermic hydrogen desorption from the carbon-carbon components to achieve optimal thermodynamics for the overall hydrogen absorption/desorption process has the potential to meet DOE targets. However, the theoretical material-based capacity is only approximately 7 wt% hydrogen, which cannot be used to make storage systems that meet the system-based capacity of 5 wt% hydrogen.
- This project is developing a materials-based hydrogen storage option consistent with DOE's long-term objective.
- This project addresses the goals of the DOE Hydrogen and Fuel Cells Program Hydrogen Storage sub-program, and attempts to tune the heat of adsorption by coupling exothermic and endothermic hydrogen elimination reactions in a cyclic system.
- Almost all of the DOE vehicular objectives are well supported, including weight, volume, release temperatures, rates, impurities, and others.
- This project is developing new materials based on light metals and aiming for a low energy transfer needed onboard (and low temperature). However, target molecules are well below the system capacity goals.

Question 2: Approach to performing the work

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

- It is an interesting and relatively new approach to thermally couple exothermic boron-nitrogen decomposition with endothermic carbon-carbon decomposition to accomplish the desirable intermediate thermodynamics. These newly tailored carbon-boron-nitrogen heterocycle compounds are new and innovative. This approach offers a viable alternative to ammonia borane (AB) liquid carriers. The approach apparently requires off-board regeneration, a logistical disadvantage.

- Formulating a liquid fuel is the right approach to potential automotive application. In theory, coupling endothermic with exothermic reactions is a good idea. However, as the principal investigator (PI) has discovered, demonstrating such an approach is major challenge.
- Seeking low Gibbs free energy materials is a very good, if rarely followed, process. The elements used are appropriate and the skills available are the correct ones. Theory-guided experiments are always encouraging to see in an approach. Unfortunately, it is not clear whether the materials considered could meet the goals if totally successful, especially as carrier liquids are needed.
- The approach to couple exothermic hydrogen release from boron-nitrogen systems with endothermic hydrogen release from carbon-carbon bonds is interesting and unique. The approach couples theory calculations with experimental work. The thermodynamic calculations are for isolated gas-phase molecules. Given the Lewis acid-base characteristics of these molecules, acid-base adducts of the starting material are likely to form (except in the case where there is a bulky ligand such as tertiary-butyl on the nitrogen), and products from the hydrogen elimination reactions will likely be oligomers (dimers or trimers). The thermodynamic calculations should be done by taking the potential for adducts and oligomeric products into account. Ignoring these interactions could lead to poor estimates of the heats of reaction, especially for the case where the universal or ideal gas constant R (in R-nitrogen-boron-hydrogen) equals hydrogen. Calculations comparing the energetics of the elimination of R-H (where R equals an alkyl group) from the R-nitrogen-boron-hydrogen species (leading to an oligomeric, probably cyclic boron-nitrogen product) versus the elimination of hydrogen from the hydrocarbon portion of the ring would be beneficial.
- The project's new direction looks at a substituted borazine analog that has improved properties compared to borazine and appears to give a clean reaction with no problematic side products. The gravimetric hydrogen storage density of 4.7% for this reaction (with R equaling hydrogen) is below the onboard vehicular hydrogen storage target. Any substitutions to the ring (or nitrogen) would reduce gravimetric density. However, an all-liquid system would be beneficial and an all-liquid system (reactant and dehydrogenated product) with slightly lower capacity would be preferred to a system with a solid reactant and/or product.
- The heat of reaction to form the cyclic borazine derivative was not provided and coupling with endothermic hydrogen release from the carbon-carbon portion of the ring was not discussed. Calculations of the heats of reaction would be beneficial to assess the potential reversibility of this reaction and any potential for coupling with hydrogen release from the carbon-carbon portion of the ring.
- This project focused on material synthesis and made significant progress.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- This project successfully synthesized new parent material. The new liquid fuel (progress after submission of Annual Merit Review slides) is promising. However, the results to date do not lead to the coupled release of hydrogen. The down-selected candidate material will not meet DOE targets for gravimetric and volumetric capacities.
- Progress has been generally impressive and participants have done well developing the first synthesis techniques to make custom carbon-boron-nitrogen compounds. Decomposition catalyst development had been quite good, but a non-PM, domestically available catalyst would be better. Relatively rapid, low-temperature decomposition (liberation of hydrogen) has been accomplished without the impurities that plague the decomposition of AB. Results give a reasonable hope of meeting DOE vehicle targets. Similar to AB, regeneration of these materials may be energy intensive and costly.
- Significant progress has been made in material synthesis; however, coupled release of hydrogen remains to be achieved. Also, the desired release of three equivalents of hydrogen is yet to be accomplished.
- This project team has finally made the compound it seeks and no longer has to use surrogates. However, all of the thermodynamic data is on surrogates still. Hydrogen release from the surrogate used a high amount of catalyst, but it released hydrogen at 70°C, which could be done with waste heat much of the time.
- The researchers accomplished the release of 1.5 equivalents of hydrogen from the parent material at 160°C. Product distribution showed no side reaction products. The strangely noisy data on desorption needs to be explained satisfactorily to ensure it is trustworthy.
- The researchers claimed that they have made a material that remains liquid at -25°C, at about 4 mole percent, but could not give details yet.

- Several catalysts were tried, but none was found to promote the second hydrogen release reaction and the proposed coupled exothermic-endothermic hydrogen release. The parent material, the cyclic amino-borane, was found to release hydrogen on heating to give a borazine derivative with preferable properties to borazine. The temperature for the release was reduced to 80°C with the presence of a catalyst. The reversibility of this reaction was not yet demonstrated and the hydrogen release from this reaction would only be 4.7 wt%. Less than this was released experimentally.

Question 4: Collaboration and coordination with other institutions

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

- This project has had good collaboration with the University of Alabama. Using theory to guide the experiment helps to narrow the selection of carbon-boron-nitrogen materials. This project had some good collaboration with the Pacific Northwest National Laboratory (PNNL) as well.
- The University of Alabama is a good collaborator that provided good theory calculation support. But it is not clear that much information or value goes back out to the University of Alabama.
- This project collaborated with the University of Alabama and PNNL.
- This project has good collaborations with the University of Alabama and PNNL. It is important to get an industrial collaborator reasonably soon. It is not too early for industrial interest to be arising, given what appears to be a viable onboard storage method with carbon-boron-nitrogen compounds.
- This project has pursued reasonable collaborations.

Question 5: Proposed future work

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

- The proposed future work is sound. The researchers need to show a credible regeneration pathway for the down-selected material.
- The proposed work is suitable, though the focus should be on high-capacity new materials, not just more.
- The future work sounds reasonable and has a good focus, but only outlines are provided and thus it is hard to judge the novelty.
- The proposed future work focuses on synthesizing more carbon-boron-nitrogen materials. The work should focus on finding a catalyst that allows for the coupling of hydrogen elimination from boron-nitrogen compounds with hydrogen elimination from alkanes. That is the unique aspect and potential contribution of this system: coupling the exothermic and endothermic hydrogen elimination reactions. The maximum effort should go toward finding a catalyst that promotes that coupling.
- Although rather broadly stated, the future work planned is very appropriate.

Project strengths:

- The PI is a very capable and knowledgeable chemist. The project seeks a breakthrough material to couple endothermic and exothermic reaction for hydrogen release
- This is an excellent goal and the method of full release at 70°C is superb (that is the waste fuel cell heat range of thermal operation). This could be delivery material.
- This project has good synthetic work.
- This is a really new and innovative material.
- This is a new approach to hydrogen storage materials and does not overlap with the efforts of any other teams.

Project weaknesses:

- Even the best of compounds are not likely to provide the correct system mass and volume. However, the work is close and still of interest because it leads the way to similar work on slightly better hydrogen density material.
- The carbon-boron-nitrogen material selected has low gravimetric and volumetric capacities and will not meet DOE's 2015 targets. There is no clear pathway for the regeneration of spent fuel.

- The calculations fail to look at oligomerization and adduct formation. The materials gravimetric hydrogen density is low and at best barely exceeds system gravimetric density targets. Efforts to couple the exothermic and endothermic hydrogen release have been unsuccessful.
- The approach requires off-board regeneration and its associated cost, efficiency, and infrastructure challenges.
- The material-based storage capacity is below 10 wt% hydrogen.

Recommendations for additions/deletions to project scope:

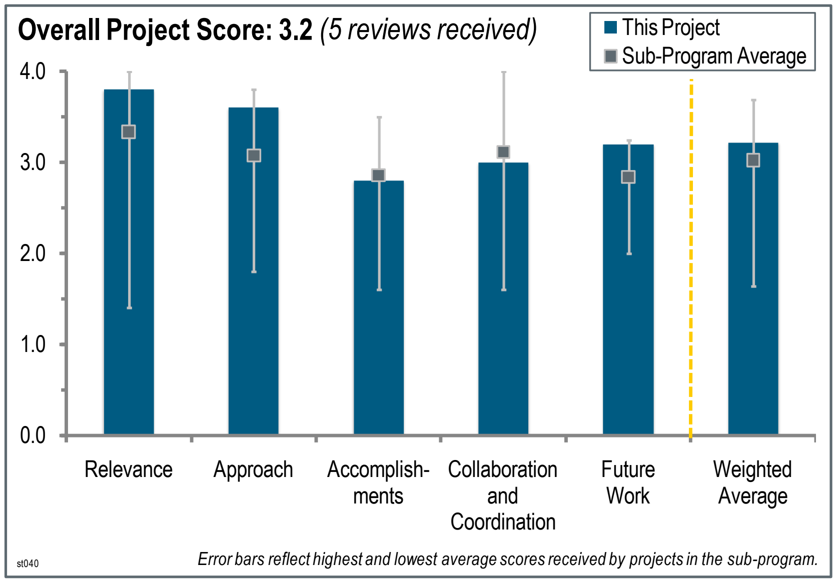
- The researchers need to demonstrate an energy efficient spent fuel regeneration pathway and focus on materials that have high hydrogen capacity.
- This project needs to move off of the surrogate compounds to the parent, and try to reduce the carrier liquid and catalyst amounts (the PI knows the need to do this). The PI should definitely focus on the spent fuel regeneration route, as this will be key.
- The PI needs to get the intellectual property rights for the new material so the information can then be shared. The source of the noisy desorption data needs to be clarified, and clean and accurate desorption data needs to be provided.

Project # ST-040: Liquid Hydrogen Storage Materials

Anthony Burrell; Los Alamos National Laboratory

Brief Summary of Project:

The objective for this project is to develop liquid ammonia borane (AB) fuels and increase the rate and extent of hydrogen release. Hydrogen carriers are to be: (1) liquid before and after hydrogen release; (2) greater than 10 weight percent (wt%) hydrogen; (3) the maximum liquid phase range for both fuel and product; (4) thermally stable at 50°C; (4) compatible with hydrazine regeneration; and (5) low cost.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.8** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project is relevant to DOE's hydrogen storage targets.
- This project has excellent relevance to virtually all DOE objectives for an onboard chemical hydrogen system. Virtually all of the critical targets are addressed.
- Developing liquid AB fuels is necessary for onboard application. This project considers many key DOE targets in its design criteria for screening and selection of ionic liquids.
- AB contains 19.6 wt% hydrogen. Identifying a proper way to release large weight percent hydrogen can result in significant breakthroughs and pave the way to meet the DOE target.

Question 2: Approach to performing the work

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

- The effort focuses on finding a promising ionic liquid as a solvent for an AB chemical hydride. Work is done in direct connection with the Hydrogen Storage Engineering Center of Excellence (HSECoE), and should therefore have a reasonable chance to achieve a commercially viable onboard system. The project is an excellent example of the synergistic combination of science and engineering.
- This project is a nice combination of engineering and fundamental science approaches in searching suitable ionic liquid(s) for AB.
- The approach is to develop liquid AB fuels by using ionic liquids to make both reactant and product phase liquids. The plan to narrow the choice of ionic liquids by using engineering design criteria is beneficial.
- This is a very well formulated approach to address the viability of liquid AB fuels for onboard hydrogen storage.
- The project should consider impurities release as one of the top design criteria. While meeting all down-select criteria is highly desirable, ionic liquids not meeting all of them are still useful and need not be eliminated.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- Significant progress has been made toward identifying the problems and partially solving them. If a working AB fuel system can be made, this project has a good chance to do so. There has been good progress in a short period of time.
- This project has identified several ionic liquids that are thermally stable up to 400°C. This is one of the most important design criteria. The next critical steps are to measure the rate and extent of hydrogen release for AB/ionic liquid mixtures and ensure that the spent fuels remain liquid.
- The results shown are very generalized. Details about the ionic liquids are lacking, and there are insufficient results from AB/ionic liquid solutions (e.g., hydrogen release data, stability data, and hydrogen storage capacity).
- Reasonable progress has been made, yet the borazine problem remains to be solved.

Question 4: Collaboration and coordination with other institutions

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

- This project has good collaborations with the University of Pennsylvania (UPenn) and various other members of the HSECoE.
- This project has very effective collaboration with Argonne National Laboratory (ANL), UPenn, and the HSECoE.
- The collaboration with the HSECoE is crucial.
- There is reasonable collaboration with the HSECoE and excellent collaboration with UPenn. A stronger interaction with the HSECoE will undoubtedly benefit the project.

Question 5: Proposed future work

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

- The proposed future work is well formulated to guide the down-select of candidate ionic liquids.
- The future work plan is good and logical.
- The future work sounds reasonable with good focuses; however, it does not have theoretical guidance for the development of effective catalysts.
- The proposed future work is logical. Given the progress to date and lack of specifics and data presented, it is not clear whether the proposed work will be accomplished prior to the end date in four months.
- With the principal investigator's (PI) departure to ANL, it is unclear if the strong progress will be maintained in the future.

Project strengths:

- The PI has extensive experience in AB fuel and the design criteria are well thought-out and implemented.
- The collaboration with the HSECoE is a strength.
- This project is an excellent combination of science and engineering aimed toward a practical onboard hydrogen storage system.
- This is a good combination of basic science and engineering approaches.

Project weaknesses:

- This project needs a stronger interaction with the HSECoE.
- Too much work is required in a short period of time (one year).
- Borazine remains a significant challenge.

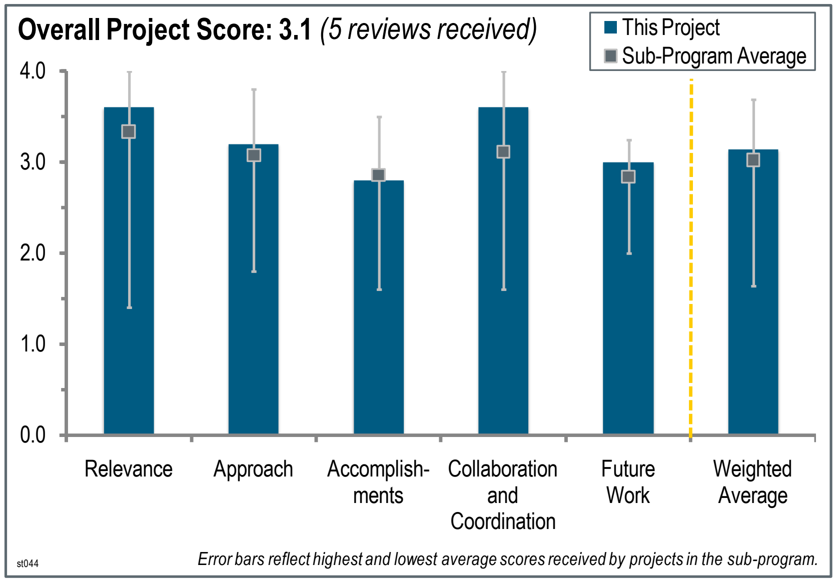
Recommendations for additions/deletions to project scope:

- This project should de-emphasize the need to meet all design criteria proposed by the PI. For example, an IL that is not compatible with hydrazine regeneration could still be selected to work with an alternative regeneration scheme.
- If possible, this project should be continued after September 2011, as all of the problems will not be solved by then.

Project # ST-044: 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) compile all relevant metal hydride materials data for candidate storage media and define future data requirements; (2) develop engineering and design models to further the understanding of onboard storage transport phenomena requirements; (3) apply a system architecture approach to delete specific metal hydride systems not capable of meeting U.S. Department of Energy (DOE) storage targets; (4) develop innovative onboard system concepts for metal hydride and adsorption hydride materials-based storage technologies; (5) design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, validate model predictions, and improve both component design and predictive capability; and (6) design, fabricate, test, and decommission the subscale prototype systems of each materials-based technology (adsorbents and metal hydride storage materials).

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.6** for its relevance to DOE objectives.

- Overall, this project is correctly focused, sensibly orchestrated, and realistic in most aspects of its approach. This project is indeed critical to the success of the DOE's Hydrogen and Fuel Cells Program.
- The project fully supports DOE objectives. The formulated aim of designing and testing metal hydride and adsorbent systems is critical to the Program.
- Hydrogen storage materials are key to improving onboard hydrogen storage systems. In this project, materials are systematically down-selected for engineering purposes.
- The Savannah River National Laboratory (SRNL) is performing this project as the lead partner in the Hydrogen Storage Engineering Center of Excellence (HSECoE) and has completed two years of effort. The primary objective of this technical contribution from SRNL is to address critical materials and engineering issues in the development of metal hydride and adsorption storage systems that can meet all of the DOE targets for fuel-cell-powered passenger vehicles. The specific roles for SRNL include serving as the system architect for metal hydride storage systems, developing models for assessing thermal management, and optimizing the designs of both hydride and adsorption configurations. As a subcontracted partner, the L'Université du Québec à Trois-Rivières (UQTR) is providing adsorbent materials expertise and testing.
- If metal hydrides or adsorbents can meet the key DOE metrics for onboard hydrogen storage, they have to do so with the current periodic table and laws of physics. The storage density versus temperature for metal hydrides and diminishing density advantage for cryo-adsorbents with increasing pressure create formidable barriers to their adoption in light-duty vehicles. Within the timeframe to adopt hydrogen fuel cell vehicles implied by the 2015 DOE objectives, advances need to occur at either a very high rate of incremental change or with significant breakthrough change. From the perspective of earned value management, much of the data, analysis, and system designs in this project may have a higher possibility of earlier commercialization in non-transportation applications, if they are scalable. DOE and the partners might do well by looking at other avenues for this research.

Question 2: Approach to performing the work

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

- SRNL has developed very comprehensive models to analyze mass and heat transfer parameters for both the hydride and adsorbent storage systems that explicitly include all of the relevant chemical and thermo-physical properties known or predicted for these sorbent materials. These models have been used to assess the performance levels for various component designs with the results being compared to the DOE storage targets for passenger vehicles. At the conclusion of phase one, none of the candidate or model hydrides (e.g., sodium aluminum hydride [$NaAlH_4$], titanium-chromium-manganese hydrides [Ti-Cr-Mn-H] or lithium-magnesium-nitrogen hydrides [Li-Mg-N-H]) can meet the gravimetric or volumetric targets required for 2010 or 2015. Similar in-depth analyses were done with the contributions from UQTR for the high-surface-area activated carbon adsorbent AX-21 that indicate somewhat better performance may be obtained with optimal design in components and bed configurations.
- The project is indeed well designed, capably managed, and thoroughly integrated with work going on throughout the hydrogen storage area.
- The general approach is effective and may lead to the success of the project; however, this depends to a great extent on a success in storage materials design and selection.
- The compiling of existing data on storage materials is indispensable and taking surrogate materials to design a system is reasonable. The heat management of adsorbent systems is critical and investigated both experimentally and computationally. These are well organized as an approach.
- In identifying the deficiencies and improvement areas for metal hydride system gravimetric densities, it would be useful to concurrently list the specific needs for improving tank designs, improved balance of plant, and heat exchangers. Also, a retrospective of the optimization for density of these components to date would help guide researchers. The hierarchal model was used to define the “acceptability envelope” for metal hydride properties for the 2010 goals. This reviewer wants to know if that model included level-above system engineering requirements that would define the envelope as well as trade-off priorities.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- SRNL and UQTR did a prodigious amount of analyses and design work to support their phase one reviews of the hydride and carbon adsorbent storage systems. Very in-depth assessments were completed and summarized on slide 24 of their AMR presentation. Nevertheless, the severe limitations with all known hydrides leads to the conclusion that no enhancement of the designs of storage bed components will ever yield storage systems that can fully meet all of the DOE targets. Possible pathways for improving performance of the carbon adsorbent storage systems were identified and analyzed. That warrants continued investigation and testing during phase two.
- The researchers’ acceptability-envelope approach and spider chart tracking are revealing the most promising paths to meeting DOE system targets for onboard hydrogen storage.
- The researchers’assessments and conclusions seem honest, realistic, and candid. One gets the impression that everything is now out in the open and the storage approaches that cannot meet the targets are being summarily eliminated from study.
- The progress in research is based mainly on the results obtained for the surrogate hydride $NaAlH_4$. These results are rather important and significant, but may turn out to be not so useful if future selections include other, more prospective storage materials.
- The pace is too incremental in the face of the goals and time available to meet them.
- The major achievements are on systems using alanate (a surrogate material containing AlH_4) with a hydrogen burner and adsorbent at cryogenic temperatures. They are not realistic for the mass production of fuel cell vehicles. The investigation should be done for room temperature materials or at least the most promising ones working at near room temperature.

Question 4: Collaboration and coordination with other institutions

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

- Collaboration with world class experts, such as Professor Chahine at UQTR, is outstanding.
- SRNL has worked extremely well with all of the HSECoE partners and other organizations that have led to comprehensive analyses of the hydride and adsorbent storage systems. In particular, a very strong exchange of ideas, concepts, and results are apparent with UQTR. All tasks appear to have been well coordinated and of great mutual benefit.
- These projects are well connected to all of the institutions that have been involved in the Hydrogen Storage sub-program for the past five years, and in many cases still are. The researchers are not reluctant to bring in new players where there is something tangible to be gained (e.g., UQTR).
- The collaboration seems good, but it is not obvious whether the team is right-sized. This reviewer asks if it is possible to identify unlikely technical, material, and system candidates earlier; focus the effort; and manage a tighter team of partners.
- Examples of collaboration are not clearly shown.

Question 5: Proposed future work

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

- The future plans extend logically from the fiscal year 2011 findings. The total system requirements, necessary performance levels, and cost factors are being more clearly elucidated and accordingly built into the system studies to increase the data base for educated go/no-go decision-making.
- The specific future tasks suggested by the SRNL and UQTR team on slide 24 of the Annual Merit Review presentation are reasonable during phase two of the HSECoE project. In particular, optimization of designs for improved thermal management supported by small-scale prototype testing would be useful and could verify the modeling predictions. Unless a metal hydride with much better fundamental properties can be identified, there is probably minimal value in further assessments for their possible use in passenger vehicles.
- Adsorbent and metal hydride material properties relate to physical processes such as heat transfer, compaction, hydrogen charge and discharge, and others. Because these are generally intrinsic properties, the reviewer asks if it is at all possible for continued heating, cooling, pressurization, flow through, charge, discharge, compaction, and other system-level testing to all be done in a simple, small-scale, quick-turnaround test device in the way that a Sieverts apparatus is, but more universal and simpler. The hope is to more efficiently identify acceptable and unacceptable storage materials and system elements, such as heaters and wall materials, before testing on a larger scale.
- Though the plans are built on past progress, they somehow repeat previous experiences. The deliverables for phases one and two differ only in their respect to 2010 and 2015 DOE milestones.
- Proper materials that have the enthalpy change of hydrogenation ranged -25 to -35 kilojoules per mole of hydrogen still need to be developed.

Project strengths:

- This project has a wide variety of collaborators, and the team is well organized.
- The staff members from SRNL and UQTR involved in the HSECoE are highly skilled and talented. The depth of analyses and creativeness of the concept development deserves strong compliments. Very thorough assessments of both challenges and opportunities were made during phase one.
- This project has a strong team, top-notch management, and a well conceived approach.
- The strength of this project is in its good fundamental basis and in the experience of the involved teams. In the case of positive development of accompanying issues, this project may succeed.

Project weaknesses:

- Unfortunately, the team does not have the proper material to design onboard tanks.
- The greatest problem lies in the fundamental properties of the candidates available as hydrides and adsorbents. Unless new materials can be discovered and developed, no amount of engineering improvement or innovation will create a hydrogen storage system that can completely satisfy all of the 2015 targets for passenger vehicles. However, some hydrides (e.g., Ti-Cr-Mn-H) could readily give storage systems that are completely acceptable for some early market fuel cell applications (e.g., specialty vehicles and backup stationary power).
- There is lots of work still to be done on this project. Representative testing, evaluation, and demonstration will become increasingly more costly, and the likely funding levels for this project in the coming years and whether there will be enough budget allocation to get the job done is a concern.
- This project has a strong dependence on the new materials design.

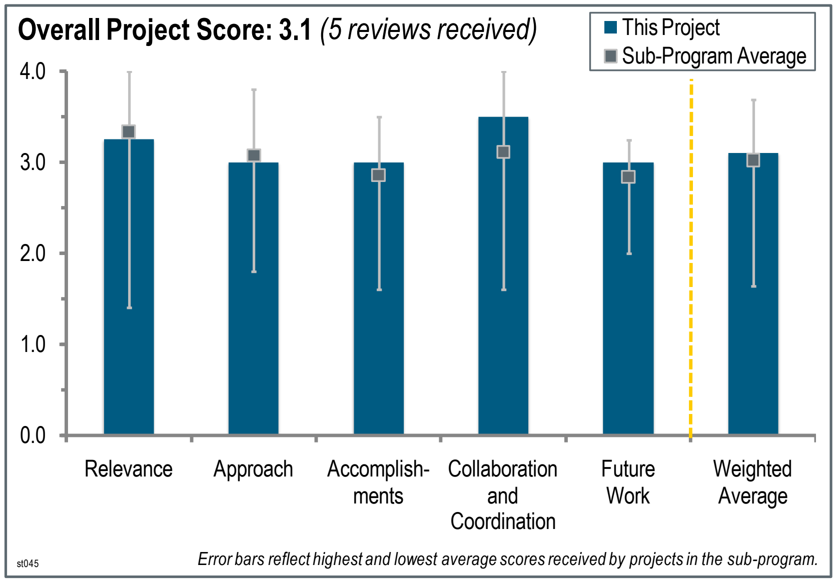
Recommendations for additions/deletions to project scope:

- It is hard to advise, but if everything develops right, this project may be a success.
- The reviewer recommends that the team continues its material research and development and hopes it will be flexible enough to take newly developed materials to other places.
- This reviewer recommends that SRNL proceed with the further development of component designs that enhance heat transfer with minimal impacts on weight and size of both hydride and adsorbent materials using small-scale testing for verification during phase two of the HSECoE project. This information should be valuable for future work on more efficient general purpose hydrogen storage systems. The researchers should not devote much more time to simulating storage systems based upon any Li-Mg-N-H compositions, as their intrinsic reaction kinetics are too slow at reasonable operating temperatures and their thermodynamic parameters will require burning substantial fractions of the stored hydrogen.
- This project should emphasize the testing of potential storage candidates on materials that can store at least 10 weight percent (wt%) hydrogen. The total system considerations will most likely dictate that a material storage capacity greater than 10 wt% hydrogen is necessary for any viable storage concept after 2015 total system requirements are properly worked into the study.
- The reviewer has an issue with slide 20. The comparison should be made to 2015 targets, as 2010 has already passed. This will make things look somewhat less promising, but that is the way it is.

Project # ST-045: 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) identify state-of-the-art concepts and designs; (2) discover and identify technical barriers to system development; (3) develop means and/or identify trajectories to overcome barriers; (4) describe and develop enabling technologies that will achieve targets; and (5) design, build, and test a subscale prototype demonstrator for the metal hydride system. The purpose and focus of the Jet Propulsion Laboratory (JPL) effort is technology management, including: (1) assessment of the current state-of-art or fitness evaluations of existing technologies; (2) identification of technology gaps on system requirements and operational demands; (3) assessment of the impact of technology gaps on the ability to develop a system; (4) up-selection of candidate approaches to device design and implementation for gap mitigation; (5) development of technology, hardware design, and analysis for up-selected technologies; and (6) continued assessment and feedback of emerging technologies.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.3** for its relevance to U.S. Department of Energy (DOE) objectives.

- The work planning and execution at JPL is well aligned with the mission of the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- The relevance of this aspect of the HSECoE to the DOE Hydrogen and Fuel Cells Program is very good. The cryogenic storage systems may be necessary if materials properties do not improve much in the near term. Thus, the design and testing of a cryogenic system may be needed for the center to meet its objectives.
- Effective onboard hydrogen storage is an important enabling element for fuel cell vehicle deployment.
- Cryo-adsorbent storage systems are one of the areas that the HSECoE works on. JPL manages the project from assessment to prototype testing.

Question 2: Approach to performing the work

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

- This project's tasks are well-organized from phase one to phase three.
- The approach descriptions in tasks one and two lack detail, but task three is adequate and sufficiently described.
- The approach involves mostly identification and assessment, with some testing mixed in. At the present and projected funding levels for this project, this is the best approach for JPL to take. Eventually, testing will have to become a larger part of the whole HSECoE enterprise.
- The reviewer is unclear on exactly what "technology management" means in the context of this project and its place in the HSECoE.
- As the cryo-adsorbent system architect within the center, JPL's approach is to concentrate on multilayer vacuum superinsulation systems for this application. Effort will be directed toward developing validated models of the

system that reduce heat loss through the vessel and improve dormancy. Initial results indicate that additional development is needed to meet the DOE dormancy targets for these systems. JPL is also designated as the site for testing metal hydride systems in phase three. It is not clear why this is so, considering that Savannah River National Laboratory (SRNL) is the system architect for this approach. This is something that can be addressed nearer to the phase three go/no-go decision point. It does not appear to have impeded JPL's efforts in cryogenic systems.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- JPL has made considerable progress toward the identification and illumination of some of the key technical barriers confronting the development of a hydrogen storage system for a fuel cell vehicle. The results of its work will continue to be important to the process of making well informed go/no-go decisions within the HSECoE. The reviewer notes that projects such as this one within the HSECoE appear to be uncovering more problems than they are actually solving. So, the effort at JPL (as in most other HSECoE projects) seems to be more in a discovery and scoping mode than in a near-to-solving-the-problem mode.
- The use of Kevlar as a wet suspension represents very good progress, as insulation is a major issue for cryo-systems.
- Accomplishments have been reasonable in the year since the last Annual Merit Review, and are certainly an improvement over the slow start to the project. The thermal insulation work has identified the need to reduce conduction through the stand-offs/support structure for the inner vessel. Hydrogen desorption heating concepts have been investigated and a flow-through heating approach was modeled to heat hydrogen from 60 to 233 kelvin (K) by the inlet of the fuel cell. The case for designing a cryogenic sorbent-based system with 200 bar capability seems unconvincing, at least from the presentation discussion. This is close to the break-even pressure; the system would be considerably simpler if the adsorbent were eliminated and the pressure increased incrementally.
- The Kevlar web-suspension approach to reduce conductive heat gain looks promising. A hydrogen recirculation loop to improve desorption heating could be a viable approach, but the impact on system cost needs to be characterized.
- The design of a cryo-adsorbent tank has been carried out.

Question 4: Collaboration and coordination with other institutions

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

- The collaboration with the California Institute of Technology, which houses adsorbent expertise, is ideal.
- The presentation slides and the presenter were very clear and specific about collaborations and how the JPL effort fits in and communicates with other parts of the HSECoE.
- This project has very visible collaboration.
- The collaborations between the center members are very good. The center has reached out to Lawrence Livermore National Laboratory (LLNL) to exchange information on cryogenic systems. The expertise of Lincoln Composites appears to be underutilized in the center.
- The clearly identified collaborators are well qualified and making significant contributions.

Question 5: Proposed future work

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

- Phase three, the prototype tank testing, is very much anticipated.
- The future plans were clearly spelled out for each task area and each phase of the project. Characterization and analysis will give way to more and more testing as time goes on, assuming the required funding is available. The presupposition of metal hydrides as a prototype demonstrator may be an unwise choice. The JPL team might be wiser to broaden its view to ensure that the efforts within the JPL project are sufficiently broadly scoped to be of at least some utility to all storage concepts still on the table.

- The proposed future work in the three JPL task areas is ambitious. The tasks include insulation characterization and subscale dormancy tests, carbon fiber outgassing, recuperator heat-exchanger testing, and mechanical testing of vessel thermal supports, plus readying the test facility for prototype testing. The team should clearly explain what additional benefit will accrue from the insulation characterization effort beyond what is already available.
- The future work is reasonably well planned and clearly identified; however, it needs to include cost work and does not have clear targets to achieve.

Project strengths:

- This project has a well qualified, knowledgeable, and experienced team as well as excellent tooling and facilities for most aspects of the analysis and testing.
- There is significant expertise at JPL in cryogenic systems.
- There is functional promise in the system design of this well executed project.

Project weaknesses:

- The presentation at the meeting had some room for improvement.
- The projected funding levels may not be sufficient enough to allow JPL to make progress on all three tasks.
- The management structure of the center appears cumbersome. From the presentation, it is not clear how the coordination and communication between JPL and other team members is managed and how effective it has been.
- It is not clear whether cost targets can be met.

Recommendations for additions/deletions to project scope:

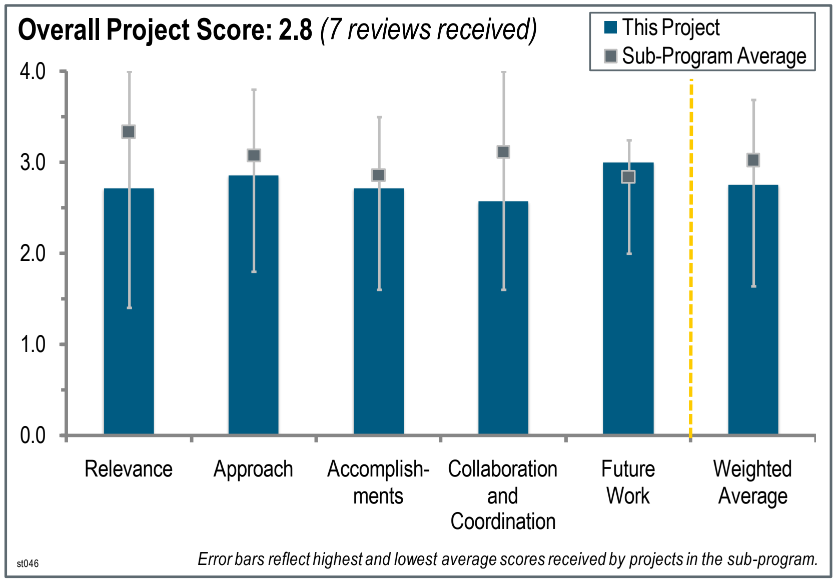
- This project should expand its interaction with LLNL. Much of the development that has gone into the cryo-compressed system could benefit the HSECoE's cryogenic systems work, particularly in the area of dormancy. It would be helpful to see, perhaps in a future presentation, the down-selection criteria metrics for the sorbent-based and metal hydride systems, particularly in light of the priority ranking of the DOE targets discussed by the center.

Project # ST-046: Microscale Enhancement of Heat and Mass Transfer for Hydrogen Energy Storage

Kevin Drost; Oregon State University

Brief Summary of Project:

The objective of this project is to use microchannel technology to: (1) reduce the size and weight of hydrogen storage systems; (2) improve the charging and discharging rate of hydrogen storage; and (3) reduce the size and weight of the thermal balance of plant components while increasing performance.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **2.7** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project is relevant to DOE goals of developing storage systems with stated gravimetric and volumetric capacities and charge and discharge rates. The project is also relevant to the goal of developing proven balance of plant components. This project is using enhanced heat and mass transfer available from microchannel devices to address the related problems in advanced hydrogen storage systems.
- This project is very relevant to DOE targets for heat transfer.
- Improvements to heat and mass transfer have the potential to significantly improve the performance and economics of storage. If the principal investigator (PI) had clearly explained why this approach was taken; the presentation would have been improved. The PI presumed that the audience knew why a microchannel system was required.
- Microchannel reactors and heat exchangers could address DOE goals of size and weight and improve charge rates for the storage applications stated for this project. The cost could be a challenge for them.
- The relevance of this microchannel technology supports the Hydrogen Storage Engineering Center of Excellence (HSECoE) objectives. However, the system designs developed by other center members do not appear to be including microchannel-based components in their designs. The reviewer is unclear how critical this technology is to the overall success of the center.
- Oregon State University (OSU) is performing this project as a partner in the HSECoE and has completed two years of effort. The primary objective of the HSECoE is to address critical engineering issues to accelerate the development of materials-based hydrogen storage systems that can meet all of the DOE targets for fuel-cell-powered passenger vehicles. The role of OSU is to employ microchannel technology that enhances heat and mass transfers within components to reduce weight, volume, and the cost of the storage systems. This project does not directly influence the composition of the storage materials themselves.
- This project is exploring a niche application for microchannel arrays as facilitators of heat and mass transfer in hydrogen storage beds and combustor/recuperator heat exchangers. Nothing has been conclusively demonstrated to date, but some promising results have been obtained. Therefore, there is an opportunity for relevance to hydrogen storage and fuel delivery systems for fuel-cell-powered vehicles. The final judgment will be decided in phase two.

Question 2: Approach to performing the work

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

- The approach has merit in several respects. Microscale devices for thermal management and mass-flow control could prove beneficial in meeting hydrogen storage system weight and volume targets, as well as fuel delivery requirements. The benefit to manufacturability (e.g., welding of small aluminum parts) and component reliability under vehicle operating conditions is still unknown.
- Microchannel technology has potential. The advantages of microchannel are obvious for liquid-liquid systems, but not so obvious for solid-liquid systems where heat transfer through solids is often rate limiting. This project assumes a non-hydrogen cooling fluid. The reviewer was not aware whether the Hydrogen and Fuel Cells Program was considering this approach.
- This project has taken the approach of using microchannel technology to develop high-priority components. The approach is clearly spelled out. It relies on optimizing the performance of a single unit cell and varying the number of cells to meet the requirements of systems of different sizes.
- This project is modeling and fabricating microchannel devices for heat and mass transfer. The researchers are developing a Modular Adsorption Tank Insert (MATI) and combustor heaters.
- OSU has identified two potential applications for its microchannel technology capabilities: (1) a MATI and (2) a Microchannel Combustor-Recuperator Oil Heat Exchanger (MCROHX). The MATI could facilitate heat transfers within the tank using compacted adsorbents, while the MCROHX could greatly reduce the size and mass of components used to burn portions of hydrogen released from metal hydrides or endothermic-chemical hydrogen storage materials.
- OSU is concentrating on two possible areas where this technology can have an impact. The microchannel material insert could save on weight and system capacity by eliminating the need for a binder. The other area is a microchannel-based combustor/recuperator to provide the heat of desorption. Feasibility needs to be demonstrated.
- This project is identifying critical component areas with shortcomings that can be addressed by microchannel plate technology (MCPT), which has led to obvious best applications for storage materials that require rapid heat creation or extraction and heat exchange. Adapting MCPT to applications by expecting physical behavior to follow model predictions may be a challenge. Throughout the reactor volume, the combustor may have some non-uniformity problems with reaction uniformity and reaction stability. Each cell is a separate catalytic reactor with a quite steep temperature gradient. In a real system, the presence of hot or cool spots could present a challenge to the reactor operation. The temperature can be controlled by flow rate as well as equivalence ratio, and the catalyst can give that a broad range far into the fuel-lean regime; however, that is only controlled in bulk and not at the cell level. The PI mentioned that the combustion cell dimensions are narrower than the quenching diameter for hydrogen/air combustion, but that is a function of temperature, hence, hot spots may be an issue.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.7** for its accomplishments and progress.

- This project has made good progress on two focused tasks. The discussion was on sorbents and what would be required to use this microchannel technology on complex hydrides. The reviewer asks whether there are other, better approaches for heating.
- In fiscal year (FY) 2011, OSU started to develop the concept of a multifunctional MATI. OSU has conducted computational fluid dynamics simulations for the integrated cooling, heating, and hydrogen distribution plates. It has built an apparatus and performed initial experiments to validate the calculated pressure drops, and has also continued to work on a MCROHX concept. OSU also formulated a computational model of the microchannel device, fabricated a unit cell, and set up a rig to test the unit cell. To date, only the pressure drops have been measured.
- OSU has developed first-generation configurations of the MATI and MCROHX and performed thermal simulations to predict behavior. Feasibility testing of a simple prototype of the MATI has started. Cost projections for mass manufacturing of these devices were made, although refinements in designs and manufacturing still remain.

- This project is still in its infancy. An assessment has been made of where microscale technology might benefit hydrogen storage system design. Some progress has been made in the design and testing of a microscale modular adsorption tank and a microscale combustor/recuperator. Temperatures near 650°C are reached in the combustor/recuperator. The reviewer asks whether there is any chance that the aluminum will reach these temperatures or if it is adequately protected from such an event, as aluminum melts near 660°C.
- It is not clear from the presentation what has been accomplished since the last Annual Merit Review (AMR). Modeling of the tank insert appears to be complete, but adsorption experiments on a representative carbon bed do not agree with the model results. These need to be reconciled. A fabrication plan has been completed that indicates that the nine kilogram insert will account for 10% of the system weight. This needs to be compared with the contribution to the bed weight from a binder. A combustor/recuperator heat exchanger has been fabricated but not tested. A combustion catalyst needs to be deposited on the channel walls and operated through numerous thermal cycles to determine durability. At two years into the project, there does not appear to be good progress.
- There is no evidence that the distributor plate is any better than a plate with drilled holes. The reviewer asks what the pumping costs (energy) associated with pumping oil through a microchannel combustor device are.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.6** for its collaboration and coordination.

- This project apparently has good collaborations with pertinent HSECoE partners. The reviewer asks how the microchannel MATI compares with General Motors' (GM's) coils and other heat exchange devices.
- In general, the collaboration between the center members is reasonable. Some original equipment manufacturer input in the two OSU concepts is mentioned, but the extent of the collaboration was not discussed.
- OSU is a member of the HSECoE and is collaborating with some members on developing MATI for the sorption system and the combustor for the hydride system.
- OSU has interacted with several of the HSECoE partners to determine what applications and advantages are best suited for microchannel technology. These interactions led to the initiation of the development of the MATI and MCROHX components. OSU has provided some of the predicted parameters for inclusion on designs and analyses of the hydride and adsorption storage systems.
- OSU is a member of the HSECoE. Some additional strategic partnerships also exist.
- For the combustor, there may be some problems in the reaction process as stated in the section on "approach to performing work." Collaboration with Sandia National Laboratories' combustion research facility may be appropriate.
- This project has limited collaboration with others.

Question 5: Proposed future work

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

- The plans for the coming year follow logically from the progress made to date. It looks like the critical technology demonstrations will be completed in phase two, which puts them in the FY 2013 timeframe at the earliest. Assuming those demonstrations are successful, the HSECoE will not be able to implement them until FY 2014—the last year for center activities.
- The reviewer generally concurs with the FY 2011 (phase two) plans presented on slide 19 of the presentation. However, fabrication and laboratory testing of the prototypes for both devices should be the main focus in order to verify the simulations of thermal performance and determine issues and problems during building and operating conditions.
- The presentation only discussed the future work to be carried out in the balance of FY 2011. OSU plans to complete the ongoing experimental activities and designs for the phase two technology demonstrations.
- The reviewer asks how MATI and MCROHX will be combined; and whether they will be combined in phase two or phase three. If students are completing the work for a thesis, it would be good to see some peer review publications. Publications are also a good review process for ongoing research.

- The future work includes completing the experimental validation of the two concepts. Assuming feasibility is demonstrated, a decision point on whether to incorporate either of these components into prototype systems was not indicated.
- Researchers need to show clearly how this system is better than traditional heat exchangers.
- For the combustor, the experimental validation needs to be on a multilayer microchannel prototype reactor with enough three-dimensionality to see if there is any sensitivity to flow and temperature non-uniformities. For the MATI, the project should do experimental thermal cycling as early as possible to validate the weldment choices for the plates and the header attachments.

Project strengths:

- The approach is well laid-out. The PI and the Oregon Nanoscience and Microchannel Institute (ONAMI)-Microproducts Breakthrough Institute (MBI) have the expertise and resources to design and build microchannel devices.
- OSU has experience with developing and fabricating microchannel technology devices for various purposes that should support its assertions that these assemblies would be suitable for those hydrogen storage components requiring improved heat and mass transport.
- This project carries with it the expertise and facilities of the ONAMI-MBI.
- The cost and weight projections for the components have been made in response to reviewer comments from the last AMR. Fabrication methods have been developed and a means of reducing costs is being investigated.
- Microchannel reactor and heat exchanger devices are valuable in many applications. The PI chose hydrogen storage applications where their strengths could be very beneficial to DOE's hydrogen storage goals.

Project weaknesses:

- There appeared to be a disconnect between the MATI design with liquid-nitrogen cooling and the flow-through cooling concept that the HSECoE lead (GM) presented as the reference design for the sorption system. There was no discussion of the microtechnology-based energy and chemical systems work carried out in FY 2010 for metal hydrides. DOE should find out if and how the work was completed.
- It is not apparent whether the as-conceived MATI and MCROHX will operate reliably under the pressure and temperature conditions that will be necessary for long-life components in hydrogen storage systems. In particular, leaks between the different fluids would be a very serious problem, as would be the manifolding of independent flow streams to external supply and removal plumbing. It is one thing for models to predict high performance behavior under idealized scenarios and an all together different situation to fabricate and assemble the suitable components for testing. Furthermore, scaling from single units to highly integrated devices could be very challenging and needs to be investigated very quickly by OSU in phase two.
- The reviewer is concerned that the definitive demonstrations of microscale methodologies will not occur until near the end of the HSECoE mission. He asks whether there will be time to translate successful test results into prototype storage system demonstrations.
- The feasibility of neither component has been demonstrated, nor has the advantage of the material insert.

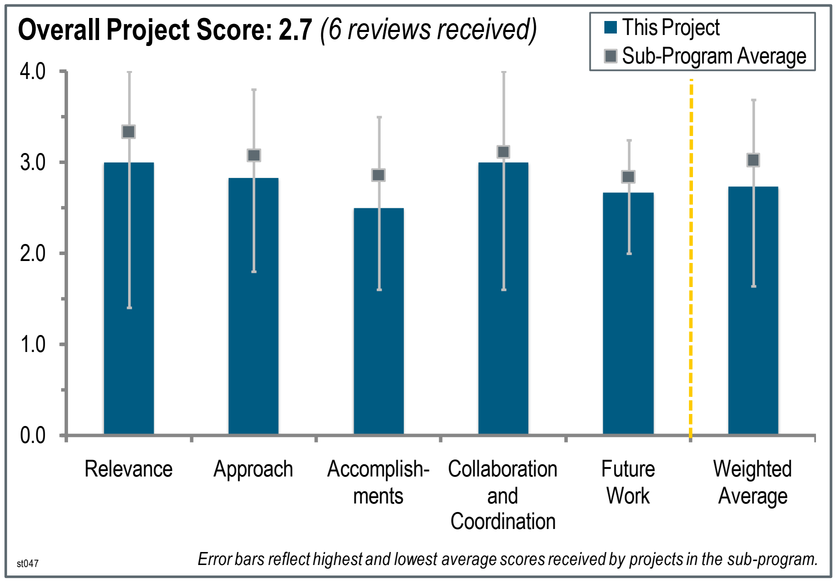
Recommendations for additions/deletions to project scope:

- OSU should focus on verifying the feasibility of its conceptual designs for the MATI and MCROHX devices through experiments as soon as possible. In particular, it should focus on the fabrication and demonstration of the integrated microchannel network for the MCROHX with liquid (e.g., heated oil) and high-pressure gases (e.g., nitrogen, argon, and helium or hydrogen) that will give complete and reliable separations (i.e., no internal or external leaks) during operation.
- This reviewer wants to know what the prospects are for completing experimental validation of the microscale methodology in FY 2012.
- The feasibility of the transition to aluminum construction from stainless steel needs to be demonstrated.
- For the combustor, which employs standard microchannel reactor geometry, it may be possible to provide an early cost estimate to see if there needs to be a greater focus on cost for the combustor as well as the MATI.

Project # ST-047: 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 U.S. Department of Energy (DOE) 2010 and 2015 hydrogen storage goals for storage systems 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 (HSECoE) partners to identify pressure vessel characteristics and opportunities for performance improvement; and (4) develop high-pressure tanks to enable hybrid-tank approaches so as to meet weight and volume goals and allow metal hydrides with slow charging kinetics to meet charging goals.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.0** for its relevance to DOE objectives.

- This project is strongly relevant to DOE's near-term targets.
- This project is directed at pressurized hydrogen gas, a key aspect of the hydrogen storage approach that has the best chance of successfully supplying hydrogen for a fuel cell vehicle in terms of range, controllable fuel delivery, and practical refilling.
- High-pressure tanks are a major enabler for improved hydrogen storage. Current technology suggests that the tanks will be the short-term solution.
- Effective onboard hydrogen storage is an important enabling element for fuel-cell vehicle deployment.
- As a member of the HSECoE, Lincoln Composites is developing high-pressure tanks for material-based systems and looking for vessel characteristics and opportunities for performance improvement. The work is relevant to DOE goal of reducing the weight, volume, and cost of onboard hydrogen storage systems.
- Lincoln Composites is performing this project as a partner in the HSECoE and has completed two years of effort. The primary objective of the HSECoE is to address critical engineering issues to accelerate the development of materials-based hydrogen storage systems that can meet all of the DOE targets for fuel-cell-powered passenger vehicles. The identified role of Lincoln Composites is to develop lighter-weight and less-expensive containment vessels that can meet the pressure and temperature requirements for these storage systems. This project does not directly influence the composition of the storage materials themselves.

Question 2: Approach to performing the work

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

- The identified development needs are well understood and the project has well conceived pathways to resolving those needs. The funding level in fiscal year 2011 ($150,000) seems rather sparse for the amount of work being done.
- Lincoln Composites has taken an organized, well thought-out approach to reducing costs.

- The work structure is investigating a number of design and material options for cost reduction, while maintaining performance and safety.
- Lincoln Composites is evaluating tank materials for cost and weight reduction as well as tank designs that meet operating requirements. Lincoln Composites is also evaluating tank durability, operability, and safety.
- This project is searching for available carbon fiber sources for testing in composite pressure vessels. Lincoln Composites apparently needs to make a tank to test the viability of carbon fiber. While this is the ultimate test, the reviewer wants to know whether there are other correlations that could be determined to accelerate comparisons, or whether there are just too few carbon fiber materials available for testing, and therefore tank fabrication is the best approach to test strength and durability.
- For the development of advanced hydrogen storage tanks, Lincoln Composites apparently has been addressing only improvements in type-IV tanks (i.e., carbon fiber wrapped with polymeric liners) for all types of storage media. The researchers have looked at some alternative carbon fibers and also considered higher-strength metals for bosses as well as designs with lower safety factors that could reduce weight and cost. There appears to have been little or no consideration by Lincoln Composites of how the interior of these cylinders is loaded with sorbent material and enhanced heat-transfer internal structures. The impact of extreme operating temperatures on the robustness of these cylinders at either cryogenic or elevated conditions was not reported with any detail during the presentation.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.5** for its accomplishments and progress.

- Progress has been made on materials for bosses, and there is a reasonable plan going forward to test carbon fibers in more detail.
- Although individual cost reductions are not large, the incremental advances add up to a significant saving.
- Progress was good but not outstanding because, for the most part, none of the issues being addressed were really brought to a close. However, the baseline design was moved to a higher level of detail; investigations of more robust materials produced some encouraging results; and studies of alternative materials, design options, and safety criteria revealed pathways for reducing the weight and the cost of the pressure vessel.
- This project designed a baseline type-IV tank with type T-700 carbon fiber, epoxy resin, high-density polyethylene (HDPE) liner, and aluminum alloy type 6061-T6 bosses. This tank is meant for service at 345 bar and -40° to 65°C gas-fill temperatures. This project is also investigating higher-strength 7075 aluminum as an alternate boss material. The researchers also tested five alternate carbon fibers and worked with two fiber suppliers. They quantified weight, volume, and cost reduction with lower safety factors and evaluated the permeation, manufacturability, and winding issues with thinner liners.
- Lincoln Composites appeared to be content to make relatively modest changes in gas cylinders using substitutions of structural materials from its baseline manufacturing designs. The researchers described selective characterization of alternative materials as a possible means to reduce the weight and cost. There did not seem to be any progress on developing a complex bed of configurations where sorbents and internal components can be integrated into hydride or sorbent beds. There was also no evaluation of potential chemical interactions with sorbent materials or other components of the polymeric liners in the storage vessels.
- Cost improvements should both be expressed as a percentage and compared to DOE targets. Fiber supply diversification, once new fibers are qualified in a design, will lead to cost reductions for materials, which is the largest cost component. This project needs to assess the appropriate qualification test changes for use of composite tanks with media inside, which should eventually lead to standards modifications. Reducing safety factors will require changes to container standards, which could take some time.

Question 4: Collaboration and coordination with other institutions

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

- There are several strategic collaborations that seem to be functioning well, and conferencing appears to be an integral part of the research and development planning and progress-tracking process. Periodic face-to-face meetings are held with the HSECoE and the coupling there seems adequate.
- This effort is supporting several other HSECoE efforts and the collaborators appear well qualified and engaged.

- Most of the collaborations and interactions are with other members of the HSECoE.
- The researchers are apparently working with others in the HSECoE, but this project does not appear to require as much collaboration as many of the others beyond sharing updated results.
- Lincoln Composites indicated interactions with a few of the HSECoE partners that seem to be mainly teleconferences on stress and pressure factors. It did not appear that the partners were significantly involved in the design studies of the conceptual storage systems other than to provide some physical properties of container materials.
- This project has limited collaboration, but the strategic partnerships, such as getting additional carbon fiber manufacturers qualified, were successful.

Question 5: Proposed future work

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

- The planned activities for the coming year follow logically from the courses of action taken in the project to date. Efforts will be made to bring ongoing tasks to closure. The emphasis of the work to date and the planned work for the coming year seems to be placed on the most critical performance factors.
- The future work is well defined and appropriate for further refining and validating the current efforts. The low-temperature work needs to be well coordinated with other HSECoE efforts.
- The proposed future work includes alternate boss material, alternate fibers, reduced safety factors, thinner liner, and alternate liners.
- The group recognizes the importance of testing at low temperatures.
- Of the future plans proposed by Lincoln Composites, those on slide 13 would be most directly useful for the phase two activities of the HSECoE partners. Namely, efforts should be on identifying and characterizing materials for operation at cryogenic and/or elevated temperatures along with assessing consequences of cycling. The processes for filling and sealing cylinders with sorbent materials are also important.
- The areas that future work will focus on were identified, but the goals were not clearly stated.

Project strengths:

- The researchers have substantial experience in type-IV tanks and carbon fiber composites.
- Lincoln Composites is a commercial vendor of high-pressure gas cylinders for a range of applications. It is expected this background would be helpful with predicting costing and manufacturing issues for hydrogen storage vessels along with clarifying safety requirements and procedures during the design phase.
- Lincoln Composites is well qualified to perform this work. The presentation was given in a scholarly, knowledgeable manner. The relevant experience of the presenter was obvious.
- This project has a good approach and has made some positive accomplishments.
- This effort is making material progress along several avenues and is contributing to a number of other HSECoE projects.

Project weaknesses:

- This project seems to be disconnected from the HSECoE objectives. All of the work so far has been for conditions typical of compressed hydrogen storage at 350 bars. Little or no work has been done to support the development of type-IV tanks for service at cryogenic temperatures (sorbents) and elevated temperatures (metal hydrides). It is not clear if HDPE or alternate polymer liners can be qualified in time for use in phase two of the demonstration effort.
- Lincoln Composites seems to have provided its HSECoE partners with limited information and support with inputs given only to the type-IV gas cylinders similar to those it commercially produces. It did not appear to consider possible contamination issues from the storage materials or how tanks need to be constructed and loaded with these sorbents. The absence of this important information was probably an impediment during phase one of the HSECoE effort.
- The project team seems underfunded for what it is trying to accomplish.

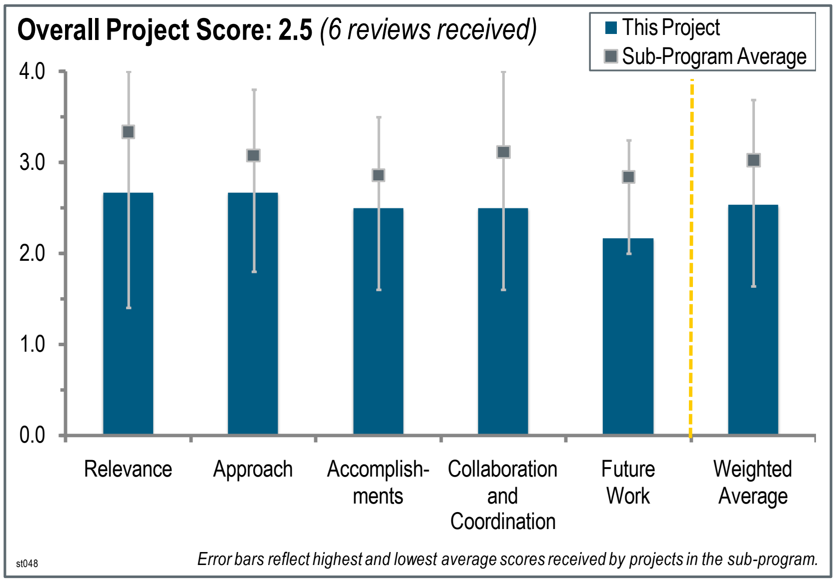
Recommendations for additions/deletions to project scope:

- This reviewer strongly suggests that Lincoln Composites aggressively addresses the design issues for assembling, filling, and sealing sorbent containing vessels. This includes looking at chemical compatibility and extensive pressure and temperature cycling. Much more interaction is needed with the three HSECoE system architects in order to support their component design and testing efforts.
- This project should focus on meeting the 2015 hydrogen storage system targets in all future presentations.

Project # ST-048: 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 U.S. Department of Energy (DOE) 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) improve the rate at which the hydrogen gas can be charged into a hydride-based hydrogen storage tank and improve the hydrogen storage density. This is being done in collaboration with the University of Delaware.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **2.7** for its relevance to DOE objectives.

- The goals are well aligned with the need to identify materials that will work. However, most of the work is retracing old ground that is unlikely to bear any new fruit. The relevance could be improved if cost or engineering aspects were at least recognized at some rough level.
- The aims of this project align with DOE objectives.
- This project's relevance spans diverse technical areas with broad objectives that aim to address critical gaps in the area of complex metal hydrides.
- This project is now working on lithium amide ($LiNH_2$)/magnesium hydride (MgH_2) systems, which have some potential. However, coordinating with the Savannah River National Laboratory (SRNL) would improve the work and better advance the science.
- The focus of this project is metal hydrides, notably MgH_2/lithium borohydride ($LiBH_4$) and MgH_2/$LiNH_2$. For the latter, the catalyst potassium hydride (KH) is used. The work is in line with DOE hydrogen storage objectives, but there is not much new being done here and, for the amount of funding, there have not been many technical accomplishments that are really new, original, or important.

Question 2: Approach to performing the work

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

- The quality of work in this project is good and, with some coordination with related projects, better progress could be made.
- A detailed approach was provided containing all of the appropriate methods to accomplish the tasks. The materials selection path appears to be significantly evolving. This is positive, as it shows the project is efficiently screening and selecting or discontinuing concepts, yet is negative in that it appears to be somewhat unfocused

and ambling. The development of quantitative selection criteria might be beneficial for more structured decision-making.

- There is poor reproducibility of the results. There are no studies of the other products of hydrogen release. The addition of KH as a catalyst only lowers the activation energy by about 2–3 kilocalories per mole (resulting in a factor of 10 in rate). It is not much of a catalyst and there is no attempt to prove that it is a catalyst. The results suggest that it is an intimate part of the reaction. The relatively high temperatures for hydrogen release for KH is common with most metal hydrides. The temperature for most of the hydrogen release is still near 300°C. Some engineering design work is being done by partners at the University of Delaware. This seems to be going far beyond what this group has accomplished experimentally. This reviewer wonders why the researchers did not use the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- This project is using the right tools and looked for and found an unexpected catalyst.
- In accordance with the comments from the 2010 Annual Merit Review, the project has less emphasis on MgH_2 and research is mainly focused on destabilized systems such as $MgH_2/LiNH_2$ or $MgH_2/LiBH_4$.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.5** for its accomplishments and progress.

- The team uses ball milling to make its materials. Some work has been done on kinetics, but only for hydrogen release, and there is no mechanistic information. The team needs to substantially improve its mechanistic understanding by determining some of the species that are formed. It also needs to run many cycles to see if it can regenerate the starting material. This reviewer wonders if it is possible with KH present. The publication productivity of the group is not very impressive considering its funding level, and the previous year's comments have not been properly addressed along with the mechanism aspects.
- This project discovered the catalytic effect of KH on $MgH_2/LiNH_2$ systems and completed some thermodynamic and kinetic work on the $MgH_2/LiBH_4$ system, though much of that work is of low value. Even though theory says using a higher $LiBH_4$ concentration relative to MgH_2 would be good, given that experiments at double the $LiBH_4$ concentration indicated no improvement, it is unclear why four- or seven-times would be of value. This project has a good rating only because this was done largely without funds for two years.
- The project is in the middle of the term and is 50% complete. However, none of the barriers have been reached so far.
- The reaction between MgH_2 and $LiBH_4$ has been well studied computationally and experimentally and its composition has been optimized (2:1 ratio of $LiBH_4$ to MgH_2, which forms $MgB_2 + 2LiH + H_2$). Therefore it is unclear what the thought process (i.e., motivation) is for studying alternate stoichiometries. In regards to the MgH_2 and $LiNH_2$ material data in the literature, the isotherms should exhibit a somewhat flat plateau with a heat of formation of approximately 40–45 kilojoules (kJ) per mole of hydrogen (10 kJ per mole lower that what is reported here). Therefore, the researchers should ensure that the points on the isotherm are actually at equilibrium and generally encourage a comparison with literature data. For the KH additions to $MgH_2/LiNH_2$, it is interesting that a drastic kinetic improvement is observed. It would be useful to further clarify the role of KH in the desorption pathway and whether (or to what extent) the beneficial properties can be preserved upon cycling. Details and assumptions for modeling work are unclear. The results appear to indicate only a few grams of hydrogen can be adsorbed for various fill times (with kilograms needed for practical systems). The reviewer asks how one extrapolates these results to a practical level and what conclusions are to be drawn from this work.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.5** for its collaboration and coordination.

- It is encouraging to see the principal investigators (PIs) are working with reputable theory groups (i.e., the University of Pittsburgh and Georgia Institute of Technology) to focus efforts on the most promising compositions.
- The team is collaborating but needs to improve its interactions with the HSECoE. It is the PI's responsibility to go down to SRNL and make this happen. The researchers are collaborating with Sholl and Johnson, who have provided computational input on the choice of metal hydride. However, because the researchers are not looking

at any new species, it is doubtful the collaboration is active, especially with the ending of the Centers of Excellence last year.
- This project has a variety of partners with different skills. The researchers have not been very successful in establishing strong collaborations with other DOE storage projects to date.
- This is the area where there is the most to gain. The reviewer suggests contacting SRNL, or maybe the DOE project manager can help organize discussions. As it appears from the PI's response to the reviewer' s comments, there is little collaboration existing in the project due to several external reasons that cannot be governed by the PI.

Question 5: Proposed future work

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

- The future work is planned logically on the base of obtained results.
- The proposed techniques and experiments are appropriate for screening complex hydride compositions; however, the majority of the specific compositions being explored and their propose are already well characterized and understood. It is recommended that the project focuses on the continued characterization of metal hydride additions to MgH_2/$LiNH_2$ materials.
- This project needs more collaboration.
- The future work is to continue to study the same systems using the same techniques that the researchers currently use. The researchers do not propose to study the mechanistic aspects, even though they have been told to do so in the past and still need to do it. They propose to use X-ray diffraction, but there is no evidence of this being done. The reviewer does not think that the project has the capability to do the mechanism development work. The reviewer asks how the kinetics can be modeled when there is no identification of rate-determining steps, a mechanism, or any structural information.
- It is not at all clear whether any new information will be gained from this $LiBH_4$ work. Thermodynamic work on an amide system is also of questionable value, as the system has already been looked at. Understanding the KH catalysis would be valuable, and concentrating all of the work on that problem would be a wise management choice.

Project strengths:

- This project found an unexpected catalyst: KH.
- This project has an improved focus on more relevant compositions and storage properties and is seeking consultation from knowledgeable theoreticians in the field.
- This seems to be just routine research.
- There are not really any strengths and this project is not doing anything original.

Project weaknesses:

- This project has many weaknesses. There is no understanding of the chemistry that is going on, a weak publication record, no original work that is not being researched elsewhere, and little explanation of the actual weight percent of the material.
- The working systems have been heavily studied and are not extracting much new value.
- The project seems to be just routine research.
- The majority of the compositions that are being explored are already well studied and there is a low probability of progress.

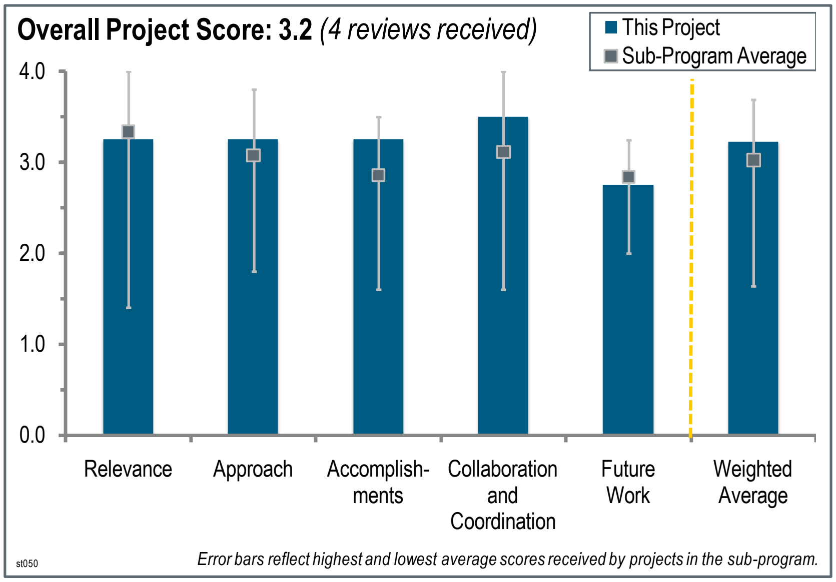
Recommendations for additions/deletions to project scope:

- This project needs to determine a mechanism and not avoid doing it. The researchers need to focus on a system and determine the mechanism. It is very important to understand the role of the “catalyst” KH. This reviewer wonders if KH is a catalyst, if the original material is regenerated, if the compounds can be recycled, and what the loss of efficiency is per cycle.

- This project needs a new system that is not extensively studied or it needs to focus on the catalytic work with KH, as that is new and not understood. Linking the PI with a kinetics theorist to help both prosper is a possiblility. DOE needs to help this project connect with others on valuable work, as they seem to not any have success making linkages (the stigma of earmark funds, perhaps).

Project # ST-050: Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

D.J. 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 U.S. Department of Energy objectives

This project was rated **3.3** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project is strongly relevant to DOE goals for sorbent materials.
- High-surface-area materials with good hydrogen binding energy are important for hydrogen storage.
- The project is relevant to DOE's overall objectives, but capacities are low compared to other physisorption materials.
- Nanoporous polymers are an important class of materials to investigate for hydrogen storage applications.

Question 2: Approach to performing the work

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

- The approach of designing and synthesizing new nanostructured POPs materials with high surface areas and then attempting to introduce higher enthalpy hydrogen binding sites is excellent.
- This project is focused on the experimental synthesis and characterization of several POPs (according to slide five, more than 100 different POPs in three different categories).
- This work has produced a massive amount of new materials; however, in many cases the planning has not been complete. For example, the reviewer questions the point of preparing the high-surface-area carborane containing POPs. There is no relationship between boron-doped carbon and carborane. The porphyrin compounds are interesting, but if each metalloporphyrin can bind one hydrogen, then it is unclear if there ever will be enough binding sites to meet DOE targets.
- The inclusion of metals to modify thermodynamics is an important area of work. However, the evaluation of kinetics does not seem to provide much benefit other than knowing that the physisorption process is relatively fast.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- This project has prepared and characterized an impressive number of materials.

- It is clear that this project has produced a large number of new materials. It would be nice if more thought had gone into the choice of some of the targets.
- Despite the excellent approach adopted in this project, none of the POPs or doped POPs materials exhibit useful hydrogen storage capacities. Nature is often quite cruel; however, the adsorption/desorption kinetics of the POPs materials are superb. An interesting result that jumps out is the high thermal stability, up to 500°C, of these materials.
- This project has made some progress, particularly in identifying which metal dopants improve enthalpies of adsorption. However, progress on increasing surface area has been only moderate, when a big improvement is required to make practical hydrogen storage materials out of POPs.

Question 4: Collaboration and coordination with other institutions

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

- This project's collaborations have been good. It is especially important to address the need for validation of measurements by other laboratories.
- The collaborations and connection with the Hydrogen Sorption Center of Excellence have been quite strong and beneficial to this project.
- The principal investigator should take advantage of others in the Hydrogen Storage sub-program and build stronger collaborations, particularly with the National Renewable Energy Laboratory. The reviewer asks if there was external validation of the hydrogen uptake data with other laboratories. This is something that the whole community can benefit from.
- The connection with computational work could have been made a little stronger, and the feedback between experiment and theory was not so clear.

Question 5: Proposed future work

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

- It would be interesting to see calculations on three-center, two-electron bonds present in carboranes to see if they predict strong binding such as in the trigonal borane calculations. Maybe there is something different in the boron-doped POPs (BPOP) species that is being overlooked. The reviewer appreciates the inclusion of experimental data for heat of adsorption measurements. The reviewer asks if everyone extrapolates to zero hydrogen coverage to determine the reported heat of adsorption (ΔH_{ads}), what the slope tells you about a specific material. For example, in slide 11, the slope of BPOP1 is steeper than the slope of either BPOP1 or 2, so extrapolation gives a higher adsorption heat, but even at low loading of hydrogen the measured ΔH_{ads} is significantly lower.
- There needs to be a task associated with improving the volumetric density of these systems.
- There is not much time left in this project, and "evaluate potential application of other emerging technologies to sorption based hydrogen storage" is not very clear. The reviewer asks what technologies are being considered.
- The project is 75% complete, so future work must be constrained to completing the ongoing studies.

Project strengths:

- This project has shown great material synthesis capability.
- There has been a notable improvement in the surface area, and thus the hydrogen storage capacity. There has also been some improvement in increasing the adsorption enthalpy.
- POPs would be ideal for hydrogen storage if they could find an approach to increase their hydrogen capacities. The adsorption/desorption kinetics are excellent, and such materials could be relatively inexpensive.

Project weaknesses:

- This project has no weaknesses.
- The surface area is too low for significant hydrogen uptake.

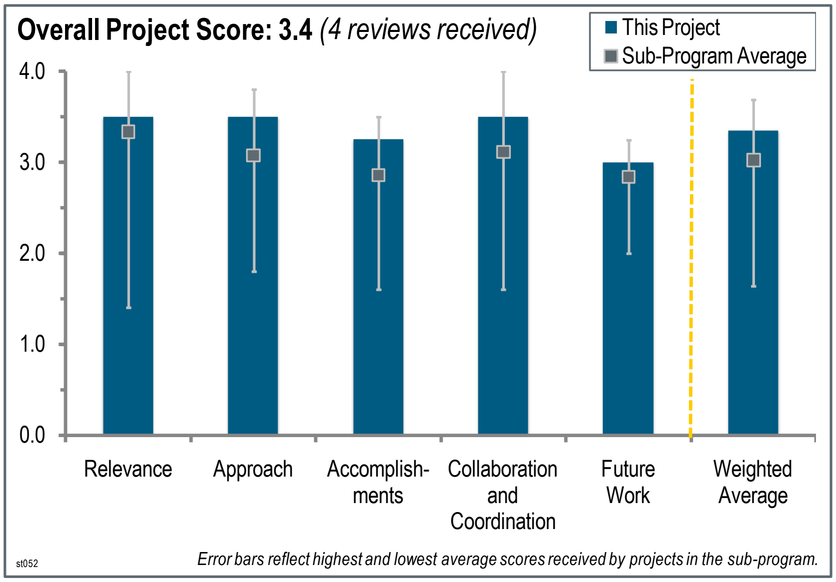
Recommendations for additions/deletions to project scope:

- The surface areas of these materials are low, and a large focus of the work should be placed on increasing the surface area.
- The reviewer recommends that a new project be initiated that builds on the results of this one. In particular, this new project should focus on the exploration of higher enthalpy hydrogen binding sites and look at a larger range of metals, as well as high-hydrogen-affinity atoms such as fluorine and chlorine. Materials of this type might also be considered for higher-temperature, fuel-cell electrolyte membranes that could tolerate steam.

Project # ST-052: Best Practices for Characterizing Engineering Properties of Hydrogen Storage Materials

Karl Gross; H2 Technology Consulting LLC

Brief Summary of Project:



The overall objective of this project is to prepare a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials. This document will be reviewed by experts in the field and made available to researchers at all levels in the U.S. Department of Energy's (DOE's) Hydrogen Storage sub-program. Objectives of the reference document are to: (1) reduce errors in measurements; (2) improve reporting and publications of results; (3) improve efficiency in measurements; (4) reduce the expenditure of efforts based on incorrect results; (5) reduce the need for extensive validation; and (6) increase the number of U.S. experts in this field.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.5** for its relevance to DOE objectives.

- This project's aim to establish the major characterization methods for engineering purposes fits very well with the objective of the DOE's Hydrogen and Fuel Cells Program.
- This project is a compilation of descriptions on the measurements, methods, and analyses based on fundamentals and practical issues for accurately determining the capacities, thermodynamic properties, and kinetics of hydrogen storage materials. Accurate results are critical to assessing the potential and limitations of hydrogen storage systems. This online handbook of "best practices" is serving a most valuable role (assuming that researchers actually adhere to its guidelines) in the search to develop better candidates in any applications. While it does not directly lead to new discoveries, conformance to the recommended procedures and attention to the caveats should decrease premature proclamations of groundbreaking materials that are based on inaccurate or biased measurements.

Question 2: Approach to performing the work

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

- The selection of subjects such as hydrogen capacity, thermodynamic properties, cycle life, and thermal properties is appropriate for the hydride community, especially for engineering applications.
- The principal investigator (PI) has been preparing and updating this how-to manual and reference book for more than four years. There have been many contributions from skilled practitioners of the different methods with a vast variety of materials and test conditions used for illustrations. The contents have been externally reviewed and updated to reflect new knowledge and observations. Currently, there are seven chapters on different topics either completed or in preparation.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The achievements of this project look fine.
- This project appears to have made significant progress, but needs to wrap up chapters and get them out for review soon.
- During the past year, the capacity chapter was updated with a new section on measuring spillover behavior and the final draft versions of the thermodynamics and cycling chapter have been independently reviewed. A new chapter on engineering thermal properties is currently in preparation.

Question 4: Collaboration and coordination with other institutions

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

- There are a lot of collaborators, and there seems to be a lot of discussion with experts of each specific field.
- This project utilizes extensive collaboration with numerous domestic and international researchers in order to obtain the most comprehensive and reliable contributions to the online documents. These interactions are unusually well coordinated.
- It would be nice to see direct input from more institutions, although the reviewer knows how difficult this is. Coordination, even between two or three institutions, where the input is largely unfunded is next to impossible.

Question 5: Proposed future work

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

- The future work looks fine, but revising the finished items such as kinetics is also recommended.
- The reviewer fully agrees with the plan to finish the chapters on thermodynamics and cycle-life properties, as well as the current National Renewable Energy Laboratory (NREL) collaboration addressing techniques for measuring spillover systems. Preparing chapters on engineering thermal and mechanical properties might not be best, as the techniques and approaches used to obtain these parameters are very different. It is probably outside the scope of effort followed during these past four years.
- The development of engineering measurement practices could be a long road with diminishing returns. It also seems that close attention needs to be paid to exactly what is available through the American Society for Testing and Materials, such as standards, and leveraging these whenever possible.

Project strengths:

- With huge numbers of collaborators from various fields of hydrogen storage materials, this project makes a significantly important report. In addition, according to the request from NREL, this project analyzes the characterization of the hydrogen capacity of adsorbents that are still under discussion.
- This project has accomplished excellent and useful work.
- In addition to the experience and expertise of Dr. Gross on the techniques covered in this project, the PI has obtained highly reputable authors on other methods, including some highly specialized ones.
- Providing the community with the methods that provide good measurement results is needed, and the work done so far is addressing those main gaps.

Project weaknesses:

- This project provides step-by-step instructions in the subject set at the beginning and at times, such as this fiscal year, it accepted urgent requests from national laboratories. There is a possibility that past subjects may become outdated if the subject field is very active.
- A reference is useful only if it is found, read, and understood, and the concepts are actually implemented. The most-novice researchers in the hydrogen storage field are probably the ones who most need to incorporate the recommendation methods, as their analyses are the most likely to miss or ignore this information.

- An enhanced emphasis on a systematic approach to improvements made from vetting and feedback is needed.

Recommendations for additions/deletions to project scope:

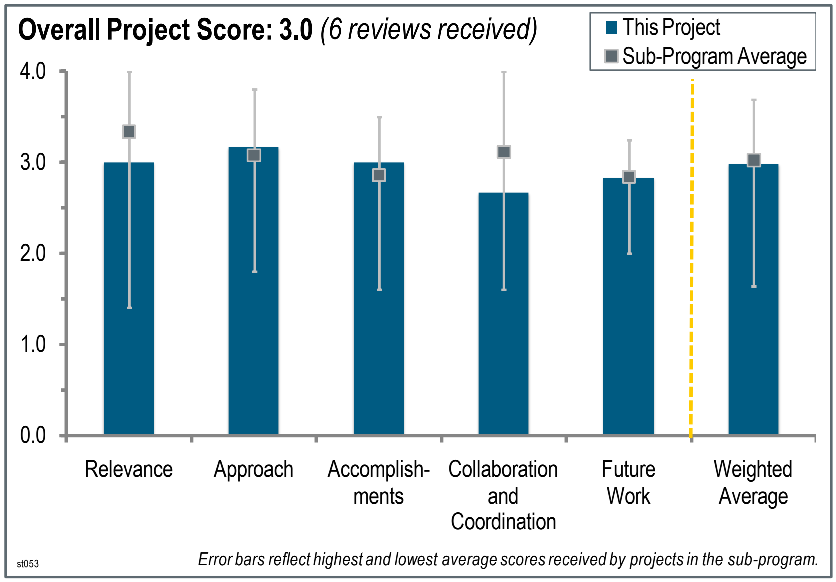
- There must be progress (from other researchers) in the subjects that this project has completed. It is recommended that researchers review all completed subjects. The kinetics chapter, for example, is very important in enabling rapid refueling and providing hydrogen to fuel cells appropriately.
- Tasks one through five (as summarized on slide eight) should be completed, thoroughly reviewed (possibly by one or more fully independent experts), and published on the DOE website and perhaps even distributed more widely via international organizations. However, this reviewer would not continue work on the two engineering chapters unless DOE has more resources to support this work. Additional new contributors, who are expert with these techniques, should be actively involved with these chapters.
- Unfortunately, the intrinsic details needed to provide good measurements have made the present, completed document rather large. Perhaps more emphasis should be placed on making a more interactive and easily used document. To provide the most use to the community, the document should be very easy for a lay-person to very quickly find the specific information needed and then to work through the issues at the different levels as needed.

Project # ST-053: Lifecycle Verification of Polymeric Storage Liners

Barton Smith; Oak Ridge National Laboratory

Brief Summary of Project:

The project goal is to perform durability qualification measurements on polymeric tank liner specimens and assess the ability of the liner materials to maintain the required hydrogen barrier performance. Milestones for 2011 are to: (1) complete thermal cycling and permeation measurements in Quantum Technologies' liner materials; (2) complete measurements of hydrogen solubility, uptake, and the effects of hydrogen-induced swelling in tank liner materials; and (3) make a go/no-go decision on the acceptability of existing liner materials.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.0** for its relevance to U.S. Department of Energy (DOE) objectives.

- The project goal is to perform durability qualification measurements on polymeric liner specimens and assess the ability of liner materials to maintain the required hydrogen barrier performance. The work is relevant to meeting DOE durability targets for cycle life and permeation and leakage for compressed hydrogen storage.
- This project provides a theoretical understanding of the permeation, diffusion, and solubility of hydrogen in high-pressure tank polymer liners. Although this is not formally recognized by the principal investigators, from an alignment perspective, this laboratory could be a routine test facility for new liner and composite variations with only a few thousand dollars of upgrades.
- This is a small project that looks at an isolated but important aspect of pressurized storage tank performance, namely hydrogen barrier performance and the overall durability of tank liner materials under anticipated operating conditions.
- This project is relevant to short-term, high-pressure tanks.
- Because high-pressure tanks are the obvious near-term technology for storage, the aging of liners is an important issue.
- The objective of this project is mainly to assess the durability of polymeric tank liners over their performance lifetime. The lifetime verification and validation of hydrogen cylinders is important, but it is unclear whether there is actually a degradation issue with these materials. This may be of a lower priority and not well aligned to the DOE's Hydrogen and Fuel Cells Program objectives.

Question 2: Approach to performing the work

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

- The approach is sharply focused on a critical aspect of the performance of pressurized tank liners. The investigators are using an approach and apparatus that could be improved upon with sufficient additional funding to allow the procurement of specific measurement instruments that would optimize how the downstream hydrogen permeation rates are determined. In truth, the investigators are doing the best they can with what they

have available to them in the way of facilities. They clearly understand the issues and the relevant parameters that pertain to tank liner performance.
- The project's approach is to verify the durability of polymeric liners in high-pressure storage tanks by subjecting specimens to temperature cycling and measuring hydrogen permeation using test protocols derived from the Society of Automotive Engineers (SAE) J2579 specification.
- The project is using direct tests of hydrogen penetration and scanning electron microscopy as well as neutron techniques to study, non-destructively, the morphologic changes that may explain it. The only possible flaw may be that the liner is tested ex situ and could lose the changes at the liner composite interface; however, this would be easy to remedy.
- The temperature cycling followed by diffusion measurements does a reasonable job of simulating fill cycles.
- The general approach of assessing the polymer material using the SAE J2579 specification is good, but could be improved by considering pressure cycles or other considerations.
- This is a reasonable approach.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- Good progress is being made on this project. The simulation conditions in terms of temperatures, pressures, and cycling rates are fully representative of anticipated vehicle operation. The investigators are exploring many possible effects, behaviors, and mechanisms that could influence liner integrity and stability. They have a good sense of what needs to be studied and why. Some of the results concerning activation energies, pre-exponential factors, and trends in extended cycling behavior are both interesting and encouraging.
- Accurate measurements have been performed and permeability rates have been measured. Based on the work done thus far, no "show-stoppers" have been identified.
- This project has made good progress by completing 4,000 temperature cycles. The permeation measurement did not indicate a degradation in temperature cycles, which was different from the expectation but is still useful for confirming the lifetime characteristics of the material. The project should consider theories regarding the relationship between activation energy and permeation.
- This project completed permeation measurements for specimens from Lincoln Composites during 4,000 temperature cycles at 430 and 860 bars and correlated changes in the permeation coefficients with the temperature and number of cycles. The researchers conducted neutron scattering measurements at the National Institute of Standards and Technology and scanning electron microscopy to look for structural changes. This project also began the solubility measurements.
- The progress of this project has not been fast, but the results are potentially powerful. The researchers identified a morphologic change by two techniques after repeated hot/cold cycling and identified metal microparticles on the surface. The fundamental values of permeation were identified (activation energy, etc.) and predictions that filled in the gaps between experiments were made on behavior versus temperature and aging.

Question 4: Collaboration and coordination with other institutions

This project was rated **2.7** for its collaboration and coordination.

- The collaboration of using materials from Lincoln Composites and Quantum Technologies is good, but further collaboration with other test laboratories that evaluate materials could benefit the project.
- Lincoln Composites and Quantum Technologies are collaborating on this project.
- This project could be improved by bringing in a polymer chemist or another researcher experienced with these tanks.
- Lincoln Composites and Quantum Technologies supply the tank liner specimens that are used in the Oak Ridge National Laboratory measurements. This seems to be the extent of the collaborations with other institutions. Hopefully key findings and results will be passed on to the collaborating companies and the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- Collaboration on this project is limited to Quantum Technologies and Lincoln Composites. It would be good to see some collaboration with the HSECoE and expanding to work with other liners.

- This project has limited collaboration. The investigators should work with a polymer manufacturer to better understand polymer properties and perhaps extend characterization.

Question 5: Proposed future work

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

- This project will complete the measurements for specimens from Quantum Technologies and the measurements for an alternate tank liner.
- The reviewer believes the researchers will try to dissolve a new sample to determine if the metals content explains the aging results. They will also close out the planned tests, as the remaining funds are low.
- The plans for the remainder of fiscal year 2011 and into 2012 evolve logically from the work that is already in progress. The measurement methodology is generally well considered and fully appropriate.
- Other liner materials should be considered along with thermal cycling relevant to materials storage (e.g., lower/higher temperatures).
- The future work could be improved by evaluating other materials besides high-density polyethylene (HDPE), and by including a comparison of the materials testing with the full cylinder results. Based on the initial results, the project should consider other stress factors and/or include the carbon fiber. It may be helpful to develop an accelerated evaluation of the permeation trend for quick screening of materials.

Project strengths:

- This project has strong expertise in materials and good availability of facilities and instrumentation.
- The method to extract fundamental values about liner, composite, and full section (joined liner and composite) to understand each part and any interface interactions is a strength. This project uses direct measurement of properties and investigates changes to the material to explain what happens.
- This project has knowledgeable investigators who are very enthusiastic. A substantial amount of work is being done on, what the reviewer considers, a shoe-string funding level. A broad spectrum of sample characterization tools is being employed to gain as much insight as possible about the effects of testing conditions on liner material integrity.
- This project could potentially create testing procedures that could be used in the future.
- This project includes a variety of tools such as activation energy assessments and neutron scattering measurements to evaluate the liner material.

Project weaknesses:

- This reviewer did not consider the project to have weaknesses.
- This project is only testing liner, which is a valid first step. The Program should also fund the rest of the required work. This project is working on a problem that is not a major concern now, though, in theory, it could be some day.
- The only weakness is that the permeation apparatus needs a certain amount of modification/upgrading to optimize its functionality and speed up its measurement capability.
- This project is limited to very specific liners.
- The project testing is unable to test the full temperature range (limited to -30°Celcius [C], which should be changed to acknowledge that the criteria in SAE J2579 is from -40°C), and does not include other stresses such as pressure. It would be helpful to be able to relate the material testing to the expected performance of complete cylinders.

Recommendations for additions/deletions to project scope:

- This project should collaborate with an analysis project (such as at Argonne National Laboratory) to develop a durability model for the tank liner.
- This project needs to add a curved frit on the test head to accommodate a section from a full tank, and then test that section and perhaps the composite alone to understand the system and the interactions fully. The researchers

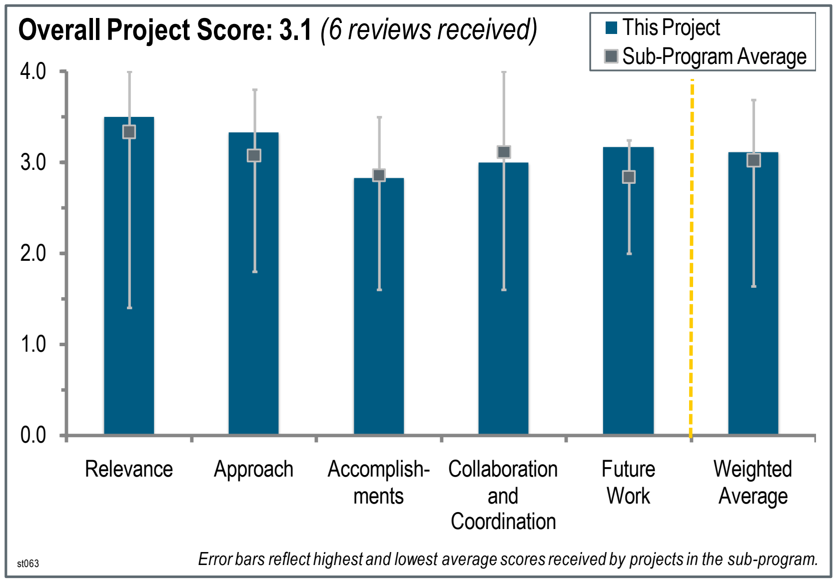
must understand where the metals seen after aging come from, Then, they should take a new liner piece and see if it has enough metal in it to account for what is seen, and if not, figure out where they come from. The researchers should consider developing this as a standard test bed so tank makers and users can test new tank designs and materials for permeation in a way that not only is standard, but also reveals the predictive variables to estimated behavior at any relevant temperature.

- This project could use a one-time allocation of instrument upgrade funding. The investigators deserve to be working with a fully state-of-the-art permeation rig that is specifically designed for the types of materials, temperatures, and conditions that require study.
- This project should consider other liners as well as thermal cycling relevant to hydrogen materials storage (e.g., lower/higher temperatures).
- Investigators should coordinate with a polymer manufacturer to verify the composition and properties of HDPE polymer. Investigators should extend lower temperatures to -40°C to simulate likely 700 bar fill conditions. Pressure cycling as well as temperature cycling may be needed.
- This project should consider developing a standard for assessing lifetime permeation or accelerated durability testing of liners. Also, the project team should expand its scope to consider evaluating the permeation of materials associated with components on a fuel cell vehicle, the cost of which could be reduced by revising its materials to plastics (i.e., fuel lines and fittings).

Project # ST-063: Electrochemical Reversible Formation of Alane

Ragaiy Zidan; Savannah River National Laboratory

Brief Summary of Project:



The overall objective of this project is to develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics that fulfills the U.S. Department of Energy's (DOE's) onboard hydrogen transportation goals. Specific objectives are to: (1) avoid the impractical high pressure needed to form aluminum hydride (AlH_3; also called alane); (2) avoid the chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as lithium chloride or sodium chloride; and (3) utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH_3.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.5** for its relevance to DOE objectives.

- Development of a less energy intensive and more efficient regeneration of desorbed AlH_3 would significantly enhance its potential as a hydrogen storage material. The electrochemical process being developed at the Savannah River National Laboratory (SRNL) may provide a viable pathway, albeit AlH_3 itself would still not be capable of being onboard reversible using the processes reported. This work has been supported for more than four years.
- AlH_3 is an important hydrogen storage compound.
- It is obvious that AlH_3 has very attractive properties for onboard hydrogen storage. The project is aimed at DOE's objectives for low-cost, efficient, off-board regeneration of AlH_3 from spent (dehydrided) aluminum.
- This project addresses the major issue with AlH_3.
- This project is of high relevance to DOE hydrogen storage objectives and sharply focuses on the regeneration of AlH_3, one of the most critical barriers for off-board regenerable materials. Both practical and technical aspects of regeneration are being efficiently explored and optimized.
- This project is focused on the economical off-board regeneration of AlH_3.

Question 2: Approach to performing the work

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

- This project has experimental methods to characterize products and reactivity, and will experiment with both sodium aluminum hydride ($NaAlH_4$) and lithium aluminum hydride ($LiAlH_4$).
- Electrochemistry has been shown to be a reasonable tool to synthesize AlH_3.
- This project approach is strong and centers around the need to overcome the high thermodynamic barriers (ultra-high pressure) required for the direct gaseous regeneration of AlH_3 from aluminum and hydrogen. The application of high hydrogen fugacity by electrochemical charging in nonaqueous solutions is very innovative.
- The general electrochemical approach to regeneration of AlH_3 is novel. The principal investigator (PI) is continuously exploring new opportunities and methods for optimizing the process, including new electrolytes,

different combinations of steps, the impact of additives, and the identification of new precursors. Elements of approach also appropriately consider practical assessments of yield, process steps, and energy consumption for each proposed regeneration pathway.
- The approach and objectives presented at the 2011 Annual Merit Review (AMR) are unchanged from those described previously with the same promises and limitations. There is no need to comment further here.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.8** for its accomplishments and progress.

- Some progress in the synthesis of AlH_3 has been achieved. However, more needs to be done in order to understand which anodic and cathodic processes are responsible for the successful synthesis. The use of dimethyl ether (DME) to synthesize AlH_3 has been shown.
- The safety advantages of AlH_3 were nicely shown. Much progress has been made in understanding the electrolytic process and making electrolytic AlH_3 in gram quantities. An effective, but undisclosed, electrocatalyst has apparently been developed and regeneration efficiency seems good. There were several possible regeneration processes disclosed in a somewhat confusing manner. It remains unclear which is the most promising. The reviewer asks if it is the DME version. The regeneration efficiency and cost are not the same. Given that relatively expensive $LiAlH_4$ or $NaAlH_4$ are involved in the process, the ultimate cost may likely be too high.
- This project looked at two reaction processes for the formation of AlH_3: using one or three equivalents of $NaAlH_4$ to form AlH_3 and hydrogen. The researchers need to compare the cost efficiency of each of the two pathways and focus on the most cost-efficient. In both cases, the researchers need to reverse aluminum metal with hydrogen and metal hydride. Case one needs to go to 100%, case two needs to go to 75% and then stop. The reviewer asks whether SRNL has performed this transformation or if it is relying on literature results. The reactions should be measured by SRNL and the efficiencies of transformation should be reported. This project also needs to provide more details on how $NaAlH_4$ is prepared from aluminum. The presentation suggested this part was easy, but it was not clear if the work was performed at SRNL or if the project is relying on literature. The reviewer also asks whether the reaction is performed in the solid state and if so, how the sodium hydride (NaH) is mixed with the aluminum. The reviewer also asks what pressure and temperature of hydrogen is required. If the reaction is performed in a solution, the reviewer wants to know what is the solvent and what are the kinetics, seeing that NaH and aluminum are not very soluble in solution.
- This project is building on the successful electrochemical regeneration results from last year (based on the formation of AlH_3-tetrahydrofuran [THF] adduct). The project is sharply focused on the detailed characterization of the entire electrochemical regeneration process, including the quantification of overall efficiency, identification and optimization of energy intensive steps, and the use of additives to improve yields. Investigating the alternative electrochemical reactions (based on use of metal chlorides) and adducts is very valuable for optimizing the regeneration process to get a complete understanding of the benefits and disadvantages of all potential routes.
- When comparing the presentations from the 2010 and 2011 AMRs, much of the same information (even virtually identical slides) was repeated. It appears that only two significant new results were presented for 2011: (1) a comparison of THF versus diethyl ether adducts (slide 16) and (2) synthesis of AlH_3 using DME (slides 22–26). It was not evident what else was done during the past year.
- The project is now more than four years old, but the extent of the improvement in the regeneration process over that time is not immediately obvious.

Question 4: Collaboration and coordination with other institutions

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

- This project is highly collaborative and appears to utilize input from key experts in the hydrogen storage field. This project is connected to the right groups whose research complements this work. Coordination with chemical industry stakeholders would be useful to understand any commercial-scale implementation issues relative to electrochemical regeneration processes identified as part of this project.
- This project has good collaborations.

- The list of collaborations is impressive, but there are no explanations as to how these collaborations function and contribute to project and DOE goals.
- This project is connected with all of the major players in the field. More work with electrochemists could be beneficial.
- The current collaborations for this project are with the same organizations as named at the 2010 AMR. There was no indication of any new contributions or interactions.

Question 5: Proposed future work

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

- The future work continues to focus on the critical barriers for AlH_3 regeneration and builds on the progress achieved to date. The particular future focus is correctly on increasing yields and efficiency through the optimization of existing strategies and the identification of new strategies relative to electrochemical AlH_3 regeneration.
- Particle size appears to be a critical parameter for AlH_3 stability and kinetics. The researchers should consult with the Brookhaven National Laboratory (BNL) to see if micron-sized particles of AlH_3 can be prepared from the electro-chemical regeneration solutions. The reviewer asks if one needs to change solvents.
- The PI addresses all of the important issues remaining.
- The future work is broad and generally useful, but not very focused. Time is running short and the best path to a commercial finish should be plotted. Scale-up experience is needed and process analysis should be started with the object of getting some preliminary costs.
- The future plans given at the 2011 AMR seem to be virtually the same as the plans shown in 2010, except they are a little more detailed.

Project strengths:

- An innovative preparation method was initially demonstrated at SRNL, along with good characterizations and some improved methods. This project has the appropriate facilities to continue more in-depth studies, which appear to be available along with competent technical staff.
- This project is focused on the right material—AlH_3.
- This is a new method of electrochemical regeneration of AlH_3, with promising chances for success.
- This project has a capable team that is sharply focused on the critical barriers with AlH_3 as a hydrogen storage medium. Tremendous progress is being made, which balances understanding at both the fundamental and practical levels.

Project weaknesses:

- This reviewer did not consider the project to have weaknesses.
- This project's weakness is a minor lack of focus.
- For some unexplained reasons, few follow-through results were reported for the past year. This suggests either a dilution of effort or that distractions arose.
- More coordination with and input from industrial chemical stakeholders would benefit the project.

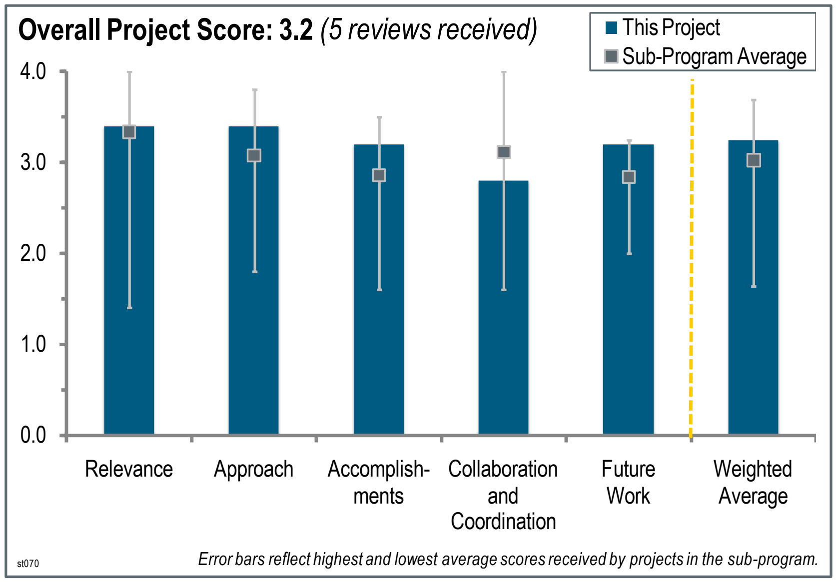
Recommendations for additions/deletions to project scope:

- The reviewer recommends that the PI either vigorously pushes forward with the future tasks given in his 2011 plans or terminates this project and goes in another direction with his research.
- This project should start some collaboration with Argonne National Laboratory (ANL) on process analysis. This would complement the very useful AlH_3 collaboration in place between ANL and BNL (projects ST-001 and ST-034). This reviewer agrees with the PI that the project is ready for industrial collaboration.

Project # ST-070: Amide and Combined Amide/Borohydride Investigations

Don Anton; Savannah River National Laboratory

Brief Summary of Project:



The objectives of this project are to: (1) perform isothermal/isobaric hydrogenation and dehydrogenation experiments to analyze the effect of composition on the kinetics of the lithium-magnesium-amine (LiMgN) system; (2) formulate an outline of discharge and charge conditions to prepare a hydrogen storage system based on the kinetics; (3) prepare a database for use by the Hydrogen Storage Engineering Center of Excellence (HSECoE) to assess the utility of LiMgN in a prototype system; and (4) modify the LiMgN system through the addition of alkali earth metals in the form of lithium-magnesium-amine borohydride ($LiMg[NH_2]_x[BH_4]_y$) for the possible formation of high-hydrogen-content bimetallic hydrogen-storage systems.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project has good relevance to DOE goals.
- The main objectives of the project are the study and modification of the LiMgN hydrogen storage systems with potential eight weight percent (wt%) hydrogen (modification of the LiMgN system through the addition of alkali earth metals). The project will prepare a database for use by the HSECoE to assess the utility of LiMgN in a prototype system. The project supports the DOE Hydrogen and Fuel Cells Program and the goals and objectives in the DOE Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program's *Multi-Year Research, Development, and Deployment Plan*.
- The lithium-amine-magnesium hydride ($LiNH_2$-MgH_2) materials are showing great promise. The lower-temperature reversibility needs to be explored in greater detail and kinetics are still a problem.
- The investigation of LiMgN as a potential hydrogen storage media with more than 8 wt% reversible hydrogen fully supports DOE objectives.
- LiMgN and modified LiMgN compounds—in the form of $LiMg(NH_2)_x(BH_4)_y$—have been shown to have thermodynamic properties and gravimetric capacity that are well suited for practical hydrogen storage applications. A detailed investigation of the hydrogen sorption reactions in these materials is complementary to the overall metal hydride research and development effort in the Metal Hydride Center of Excellence (MHCoE), and is closely aligned with the research, development, and deployment objectives of the Program.

Question 2: Approach to performing the work

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

- This team is working well to advance this class of materials, and long-term reversibility needs to be demonstrated.
- The methods and procedures planned to be used in the research are sufficient for the successful implementation of the project.

- A logical and well designed approach involving material synthesis and analysis, characterization of reversible sorption reaction behavior at different temperatures and pressures, and cycling characteristics has been employed in this project. The approach is well focused on the key technical questions that must be answered to fully evaluate the usefulness of this material system in practical hydrogen storage applications. A good connection with related work conducted in the MHCoE (Z. Fang, U. Utah) has been established. This is allowing the information gained from studies of these materials to be readily transferred to the HSECoE.
- The project uses the experimental measurements to determine the kinetics of hydrogen release and uptake in LiMgN materials with dopants. Some insight into why or how additives were selected would be interesting.
- The approach involves a standard set of measurements and material synthesis, and explores the effects of milling and modifiers. The target system magnesium amide ($Mg[NH_2]_2$), with large additions of lithium borohydride ($LiBH_4$), is also explored.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- This project has done very nice work measuring kinetics for release and uptake of 2–3 wt% hydrogen under isothermal conditions. More groups should use this approach. It would have been helpful to see the kinetics at higher conversion. The assumed five kilogram hydrogen capacity and average rate measurements show the release time to be more than 30 minutes. The reviewer asks whether this was assuming 8 wt% hydrogen. It is a little difficult to follow, as the temperatures used in the study appear to give approximately 2–3 wt% hydrogen in the first 30 minutes. The reviewer asks whether there are any results from non-ball milled samples, prepared by high-pressure methods.
- Good progress has been made in 2010 and 2011 on isothermal and isobaric kinetic studies of hydrogenation and dehydrogenation in LiMgN. Especially interesting results have been obtained on the effect of milling conditions on charge and discharge rates as well as differences in hydrogen sorption reaction pathways at low and high temperatures. Although the enthalpy and capacity of the materials are promising for a practical storage system, the slow sorption kinetics in this material remain a serious challenge. Interesting results have been obtained on the new amide/borohydride materials. The addition of $LiBH_4$ to $Mg(NH_2)_2$ was shown to lower the desorption temperature significantly and greatly reduce the amount of ammonia release compared to the pure amide compound. This result is particularly intriguing because it may provide a pathway to the identification of a related compound with improved sorption characteristics. Although technical accomplishments and progress were made in many areas in 2011, the remaining technical barriers and their potential impact were not clearly identified in the presentation. It, therefore, was difficult to assess whether or not the principal investigator and his team consider these systems to actually be viable candidates for a practical storage system.
- Cycling at lower temperatures appears to be helping the reversibility of these materials; however, rates of hydrogen release need to be addressed. Hydrogen release rates are not just another target; they are a primary target. It does not matter if every other target is met—if the hydrogen cannot get out faster, this material will not make it.
- This short-term project is going according to schedule. The milling technique, discharge temperature, and modifier composition influence on initial hydrogen and ammonia discharge temperatures as well as sorption rates were studied.
- For the LiMgN system, SPEX milling showed improvement from Fritsch milling. Oxide modifiers have lowered the initial hydrogen release temperature and the amount of ammonia release. Magnesium nitride (Mg_3N_2) formation predominates in high-temperature cycling. Mixtures of $Mg(NH_2)_2$ with $LiBH_4$ have shown a decrease in the dehydrogenation temperature and an increase in the amount of hydrogen released.

Question 4: Collaboration and coordination with other institutions

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

- The collaboration with investigators in the MHCoE has been valuable. Likewise, the close connection between this project and the engineering efforts in the HSECoE is useful and important for both projects.
- The results of the project are added to the HSECoE database. The level of collaboration in the project appears sufficient.

- This is an independent project with little discussion on external collaborations. Collaborations have started with theory groups at the Georgia Institute of Technology and the University of Pittsburgh. The reviewer asks whether there are any concerns with the heterogeneous nature of samples for Raman analysis or with the consistency of the spectrum with sampling. The reviewer also asks if there are any collaborations with the University of Nevada, Reno on the choice of gas feeds for prolonged cyclability.
- So far this project does not have any strong collaborations or theory guidance. The generated data in this program is being directly imported into the HSECoE database and is being incorporated into parametric equations to guide system design.
- This project needs more help with understanding the apparent phase changes on cycling. It is good to see more theory collaboration coming next year.

Question 5: Proposed future work

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

- The future work is well planned and appears logical considering the results obtained.
- The future plans are straightforward extensions of the work reported this year. The plans seem to be well formulated and focused on important issues raised in the project to date. However, it would have been helpful if the key technical hurdles and challenges had been explicitly identified. That way, the future plans to address and mitigate those problems would be more compelling.
- This project is ending. It had a nice run with useful results.
- The proposed future work will continue exploring $LiNH_2$-MgH_2, the role of additives, and the role of ammonia release. Collaboration with the Georgia Institute of Technology and the University of Pittsburgh is planned to couple experimental results with ab-initio calculations to identify kinetic enhancing mechanisms.
- Ammonia release is still an issue, but unless kinetics can be improved, these materials will not be down-selected. A better focus on rate improvements is called for.

Project strengths:

- The project investigates potentially useful material and provides a database for the HSECoE.
- This project has a great team and is making clear progress.
- This project has a strong technical team experienced in all aspects of materials synthesis and reaction characterization working on this project. The team has a close connection with the HSECoE. This provides a strong focus for the ongoing work.

Project weaknesses:

- The study shows persistent formation of the Mg_3N_2 phase, which may severely limit the cycling capability of the material. It is also not clear how the formation of ammonia will be addressed.
- Slow kinetics remains to be a serious problem with the materials being investigated here. It is not entirely clear what is being done to address that challenge. Ammonia release from the amine materials is another outstanding issue. Although some progress has been made with the incorporation of ammonia-inhibiting additives, it is not apparent whether this approach will ameliorate the problems with ammonia release.

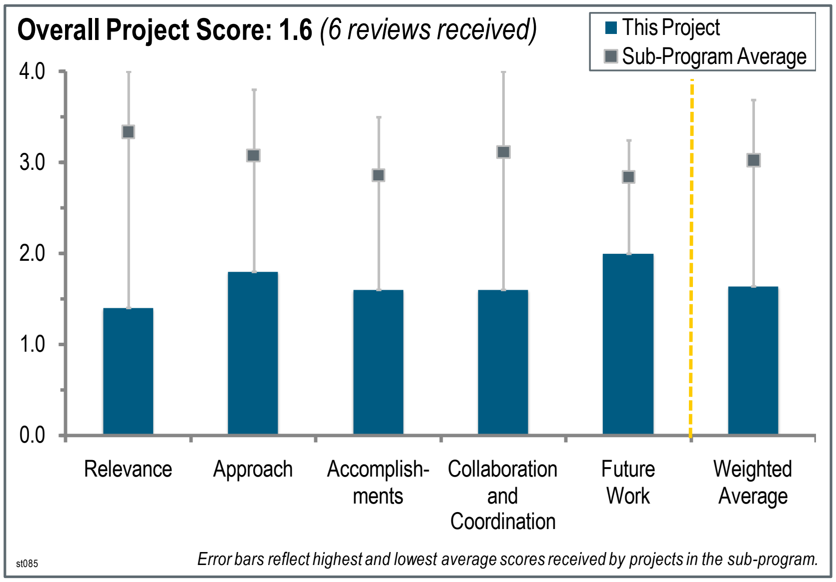
Recommendations for additions/deletions to project scope:

- The project should focus on rates at lower temperatures.
- A more keenly focused effort on improving sorption reaction kinetics is needed. This seems to be the most serious issue, and it should be a primary area of emphasis going forward.

Project # ST-085: HGMS: Glasses and Nanocomposites for Hydrogen Storage

Kristina Lipinska-Kalita; University of Nevada, Las Vegas

Brief Summary of Project:



This is a Congressionally Directed Project that includes facility development. The ultimate goals of this project are to extend the concept of glass-based materials as hydrogen storage media and to demonstrate a pathway to finding a class of materials for hydrogen storage media that can hold hydrogen at ambient conditions through physisorption. This is an extensive research project in the physics and chemistry of glasses and of glass-based nano-crystalline materials. It seeks to fill gaps in the current understanding of these complex materials and shed light on nucleation and crystallization phenomena in glass matrices to extend their technological applications. The objective for the current project year is to develop glass-based materials with structural properties that would make them promising candidates for use in sponge-type hydrogen storage.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **1.4** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project stated that it will address the discovery of new hydrogen storage materials, which should make it relevant to DOE Hydrogen and Fuel Cells Program technical objectives. However, the project began in November 2009 and, to date, has obtained essentially no technical results.
- Although hydrogen storage is obviously a very important topic in meeting objectives, this work is very fundamental in nature and not focused on implementation. For example, the principal investigator (PI) discussed heating the glass structure to aid hydrogen absorption and desorption, but no analysis of energy usage was planned. This project appears to be a very high risk.
- This project has focused on facility building thus far, rather than hydrogen storage research.
- The materials described as targets do not have a path to follow to meet DOE targets.
- A compelling case has not been made as to why glass-based materials are anticipated to be promising hydrogen storage or delivery media. If a glass matrix could actually serve as a “sponge” for hydrogen, then that would be an important development. However, that has not been supported theoretically or experimentally. Also, the gravimetric and volumetric capacity penalties introduced by the glass matrix have not been addressed. At this stage, this is a highly speculative project and it provides only marginal support to the Program.
- Until the PI can show that there is an identifiable pathway to competitive hydrogen storage materials and methods from this project, there is not a clear indication that this project supports the Program’s goals for improved hydrogen storage.

Question 2: Approach to performing the work

This project was rated **1.8** for its approach.

- The approach focuses on using amorphous and nanocrystalline glass structures as hydrogen storage media. The glass serves either as a stand-alone “sponge” for hydrogen or as a host for dopants or other additives, which would facilitate the binding of hydrogen within the framework. Presumably the vacancies, defects, and dangling bonds in the glass would serve as adsorption sites. However, virtually no theoretical or experimental support is provided that would form a foundation for this approach. The reviewer asks, for example, if the diffusivity of hydrogen in different types of glass has been measured, and if any prior work has been reported on the absorption and retention of hydrogen as a function of temperature in a glass matrix. The approach as currently stated is highly speculative and lacks a solid foundation. The complementary approach using glass microspheres was mentioned; however, that approach is far different than the one given here, and does not provide any meaningful support to validate the present work.
- The proposed approach is vague and only generally described as a study of using glass composites to support storage materials or as microspheres for hydrogen containment. There is a lack of specific details, making it impossible to judge the merits of the approach. Four tasks are listed for the proposed approach, and the first task is nontechnical as it deals with establishing a laboratory and procuring equipment. The remaining tasks are no more than 10% complete.
- The approach of exploring the high free-volume characteristics of glass materials for hydrogen storage is an interesting one, although gravimetric capacities may be inherently lower in silicon-based glasses. However, it appears that the PI regards the objective of this project to be more related to studying the basic aspects of free volume in glass rather than investigating hydrogen storage in free-volume glasses.
- The approach is very unclear. A few statements were made that the project hopes to create and identify some form of amorphous glass with nanocrystals or open structure that may or may not be formed and where hydrogen may or may not be physisorbed at significant number densities.
- During the first 18 months of this project, the laboratory was constructed and the $300,000 Raman spectrometer microscope and the krypton-argon laser were purchased. However, the PI did not appear to do the groundwork research needed to suggest that the properties of glass actually have the potential for storing hydrogen as described in the “Approach” slides. The laser, Raman spectrometer, and microscope are the diagnostics to study glass materials with open structures or nanocrystals, or that are functionalized with dopants. This reviewer is concerned that a preliminary study of the hydrogen storage potential from first principles and known material properties, mixed with mobility and kinetics modeling, could indicate that there is no need for the diagnostics if there is no potential for the modified glass to store hydrogen at practical or interesting levels.
- The permeability of hydrogen in glass requires very thin membranes and high temperatures (greater than 250°C). Microspheres are glass bubbles on the order of 100 microns in diameter with very thin glass walls (0.5–1.5 microns). The time constant for transport of hydrogen through the very thin wall is parts of an hour. Irrespective of any features within the bulk glass that may adsorb hydrogen, the kinetics from the mobility of hydrogen within the glass structure could make this storage method uncompetitive.
- This year’s work has focused on building and equipping a laboratory. No progress on materials work has been achieved.
- Limited data was presented, as work has been significantly delayed. It appears to be a “try-and-see” approach.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **1.6** for its accomplishments and progress.

- The majority of the progress thus far has been in the construction of a laboratory and the acquisition and testing, synthesis, and measurement equipment. Very limited work has been done on the initial fabrication and characterization of a series of glasses that will be used in the project.
- Most of the progress to date has been directed at establishing the experimental facilities to conduct the proposed work.
- The main accomplishments to date are the laboratories that were setup and the purchase of major diagnostic and glass development equipment. In addition, there was the synthesis of three glass samples each doped with a different network producer or modifier metal to create potentially nanocrystal nucleation sites. Subsequent X-ray

diffraction analysis indicates the potential for nanocrystals within the glass. However, there is no evidence of a demonstrated theoretical basis relating the nanocrystals to hydrogen storage.
- Other than outfitting a new laboratory, very little progress has been made. Apparently, several batches of glass composites have been made, but no technical progress on demonstrating the glass composites' applicability as a viable candidate for use in a hydrogen storage system was made.
- This project has been significantly delayed and the only real progress to date has been laboratory modification, equipment purchase, and personnel hiring; all of which might be required, but none of which truly benefits DOE in reaching its goals.
- This project has made no technical progress.

Question 4: Collaboration and coordination with other institutions

This project was rated **1.6** for its collaboration and coordination.

- Unfortunately there appears to be no collaboration with any person or organization familiar with hydrogen storage or with prior DOE-funded research on hydrogen storage in glass structures. All of the other collaborations appear to be related to setting up a diagnostic facility for glass-related research and development.
- Collaborations with institutions specializing in glass synthesis (Coe College) and characterization (Lawrence Berkeley National Laboratory; Argonne National Laboratory; the Illinois Institute of Technology; and the University of Verona, Italy) are mentioned. However, at this stage of the project, it is difficult to ascertain the importance or value of those collaborations. It is strongly suggested that the PI collaborate with a research and development group that has expertise in the details of hydrogen uptake and release measurements (especially using the Sieverts apparatus).
- This project has had minimal collaboration outside of the university.
- There is little or no evidence of potential collaborators for this project.
- This project has no collaborations.
- The PI needs to collaborate with someone who has relevant background in hydrogen storage in glass.

Question 5: Proposed future work

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

- The future plans include the synthesis and processing of glass structures, microstructural characterization of the materials, and synthesis and testing of nanocrystalline composites. However, no plans are provided concerning the introduction of hydrogen into the media and the characterization of hydrogen sorption reactions. This is an obvious and serious problem that must be corrected.
- This project needs to focus on DOE targets and do some related work.
- The proposed future work does not appear to have a foundation for understanding the physics and thermodynamics that would govern the transport of hydrogen into and out of glass media or govern the storage itself. These properties include hydrogen mobility, permeability of glass for hydrogen, the anticipated storage reversibility, volumetric and gravimetric density as a function of nanocrystal, defect, inclusion, open pore number density, or any other potential property that could be considered in this project.
- The permeability of hydrogen is described in the glass microsphere projects that the PI references as a motivation for this project, yet the models were not employed to learn whether or not permeability is a showstopper. A good example of the lack of forethought can be seen in slide 20, where the proposed work is a sequence of material synthesis and measurements of properties, but without the offer of any theory suggesting a mechanism for hydrogen storage. Task 4.0 Milestones M.4.2 and M.4.3, for example, are where the PI looks for the material of nanocrystals.
- Now that the experimental facilities have been constructed, the project will begin some actual significant experimental work.
- Essentially all of the technical work still needs to be done, and the original technical plan still needs to be executed. This project is scheduled to be completed in October 2011.

Project strengths:

- The main focus of this project is the synthesis and characterization of glass matrix structures and nanocrystalline composite materials. The PI and the team seem to be well qualified to conduct that work.
- Glass is a class of materials that may have potential for hydrogen storage because of the inherent levels of high free-volume.
- The PI is very experienced in the physics and material science of glass.

Project weaknesses:

- No work on hydrogen storage is actually planned. The project is focused exclusively on the synthesis and testing of glass structures. The introduction of hydrogen into the media and the characterization of hydrogen sorption processes are not mentioned in the future plans.
- The PI has little or no background in hydrogen storage. There does not appear to be a sharply focused strategy for increasing the hydrogen storage capacities of high free-volume glasses.
- The previous work on glass microspheres as a potential containment source for hydrogen has been completed. Duplication of those studies would not likely contribute to hydrogen storage technology.

Recommendations for additions/deletions to project scope:

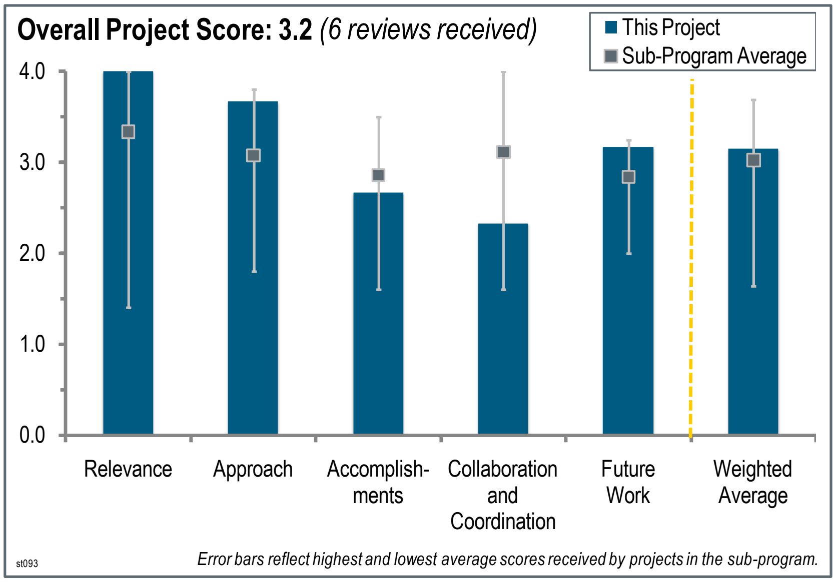
- This project should focus on hydrogen storage properties in the glass media and initiate collaboration with groups with expertise and capabilities in hydrogen sorption measurements (e.g., Dhanesh Chandra at the University of Nevada, Reno)
- This project should begin by investigating the baseline hydrogen storage properties of pure silica glass. The researchers should then establish a collaboration with Dhanesh Chandra at the University of Nevada, Reno, who is an expert in hydrogen storage in materials.
- There does not seem to be a logical science- and engineering-based plan to execute this project. There is no test plan, and it is recommended that the PI develop one. However, the plan should not simply use the glass making and Raman diagnostic tools to employ trial and error methods to find out if there are hydrogen storage opportunities with this project's approach to glass. The test plan should be reviewed by DOE hydrogen storage experts before the experimental phase of the project continues. A good start would be to develop a model for identifying the potential characteristics of modified glass that would be necessary to meet the DOE's hydrogen storage goals, and then identify known mechanisms and prior DOE hydrogen storage material science that are applicable to this project's approach. Questions to be answered and should have been answered in the project's last 18 months include;
    - What adsorption mechanisms with hydrogen and glass (with or without dopants) are possible.
    - What the known physics and thermodynamic relationships are that characterize the adsorption.
    - What the potential number densities of nanocrystals or other distributed hydrogen storage sites are.
    - How much hydrogen is needed at each site to compete for gravimetric and volumetric densities with current state-of-the-art hydrogen storage sorbents or metal and chemical hydrides.
    - What the implication is on storage kinetics of hydrogen solubility, diffusivity (permeability), and mobility in the bulk and modified glass.
    - Whether the answers to these questions lead to a justification of continued research in the project's current direction.
- This project needs to evaluate the energy cycle to determine the efficiency of the hydrogen storage process.
- This project should not be continued.

Project # ST-093: Melt Processable PAN Precursor for High Strength, Low-Cost 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 by means of: (1) significant reduction in the production cost of the polyacrylonitrile (PAN)-precursor via hot melt methodology; and (2) the application of advanced carbon-fiber conversion technologies development at the Oak Ridge National Laboratory (ORNL) to down-selected formulations.



Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **4.0** for its relevance to U.S. Department of Energy (DOE) objectives.

- Low-cost manufacturing techniques for high-strength carbon fibers are an important enabler for the commercialization of hydrogen fuel cell vehicles.
- This project is aligned with current products and the early market as well as the development of the long-term launch of vehicles later in the decade.
- The project is well aligned to DOE Hydrogen and Fuel Cells Program objectives, as it focuses on the reduction of carbon fiber cost for hydrogen pressure vessels. It is clear that carbon fiber is the key cost driver for pressure vessels, and the precursor is the dominant cost in the carbon fiber. This project correctly focused on the critical path of reducing the cost of the cylinder through an alternative precursor manufacturing approach.
- ORNL is developing the melt-spun PAN precursor technology to reduce the production cost of high-strength carbon fibers by approximately 30%. The project is highly relevant to DOE's objective of reducing the cost of onboard storage systems. Melt spinning also has the potential to reduce the manufacturing cost of carbon fibers and to increase the production rate. Because carbon fibers account for about 75% of the cost of the compressed gas storage systems, success in this project can bring down the cost substantially.
- Reducing the cost of carbon fiber is critical, as shown, for example, in the analyses reported in ST-002 and MN-008.

Question 2: Approach to performing the work

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

- The melt-spun approach is well formulated and has been partially proven by BASF Corporation (BASF) in the 1980s. This project seeks to improve the melt stability by reducing the wet temperature below the PAN degradation temperature. In partnership with Virginia Tech, ORNL is investigating polymer chemistry to generate the proper polymer feedstock and a novel spinning approach to generate the filaments.
- The approach builds upon the melt-spun PAN precursor process identified by BASF in the 1980s and attempts to resolve the key roadblocks preventing this technology from becoming a viable manufacturing process. ORNL has the unique capability of evaluating the process from the precursor development to the carbon fiber conventional pilot line.

- According to the analysis of ST-002, more than 40% of carbon fiber cost comes from the fabrication of the precursor. This project aims to establish a completely new method to make the PAN precursor.
- The melt-spun process can indeed significantly lower the production cost of the fibers. This project is aimed at addressing the key technical issue of the melt-spun process by reducing the melt temperature below the PAN degradation temperature.
- This approach is feasible in theory and would reduce costs if successful. However, not checking the quality of the resulting carbon fiber may result in a good PAN fiber, but one that makes a bad carbon fiber.

Question 3: Accomplishments and progress towards overall project and DOE goals

This project was rated **2.7** for its accomplishments and progress.

- Good progress has been achieved in developing and characterizing benign plasticizers to melt-spin PAN and promote a higher degree of drawing and novel ion-containing co-monomers and ter-polymers. ORNL and Virginia Tech have demonstrated initial spinning with a hydrated melt of 95 to 5 acrylonitrile to methyl acrylate and drawn 10–20 micrometer diameter filaments. Cost modeling from the past year shows a potential of an approximately 31% reduction in carbon fiber costs compared to the conventional wet-spun method. However, the true gain cannot be quantified until the tensile strength and modulus of elasticity of melt-spun fibers are measured.
- The reason why only a few companies can make high-strength and lightweight carbon fiber is that these companies are originally spinning companies and are rich in experience and technology to control synthetic fibers. Considering the budget and manpower of this project, the achievement is wonderful.
- This project is making good progress in the precursor development.
- This project demonstrated the melt-spun PAN precursor fiber. However, there is no determination of the tensile strength and the fiber translation efficiency.
- There is still a lot to accomplish, but the project is melt-spinning PAN fibers using suitable feedstocks.

Question 4: Collaboration and coordination with other institutions

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

- Virginia Tech is a partner in this project. The project also leverages funding from the DOE Office of Energy Efficiency and Renewable Energy's Vehicle Technologies Program.
- Conversation with stakeholders is recommended.
- There is little collaborative effort presented, although there might be more effort existing as an informal collaboration.
- It is not clear how much value comes from the noted collaborations.
- The project has limited collaboration and would benefit from having an industry partner or connection to confirm the melt-spun precursor will be a successful product.

Question 5: Proposed future work

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

- The future work plan is a logical progression from the previous work. The achievement of melt-spun PAN copolymers with comparable characteristics to wet-spun precursor fibers will be a significant milestone. The trials of oxidation and carbonization should be included in this future work.
- The proposed future work seems to be fine, but much more collaboration will be needed.
- The work plan looks good and reasonable.
- The proposed future work is suitable.
- The future work calls for a continuing generation of acceptable hot-melt PAN filaments/tows for the remainder of fiscal year (FY) 2011, and process improvements and conversion in FY 2012.

Project strengths:

- The principal investigator (PI) is highly experienced in carbon fiber development, and ORNL has excellent facilities. This project benefits from past involvement in carbon fiber projects and funding from other sources. The project has the potential to make a significant contribution toward reducing carbon fiber costs for compressed gas systems.
- The strong point of this project is its efforts to establish a completely new technology to make a high-quality precursor of carbon fibers to be used for an onboard compressed hydrogen tank.
- A significant intellectual property portfolio in carbon fiber has been developed.
- As previously indicated, this project is focused on the critical cost reduction opportunity for hydrogen tanks. The project topic is a key strength and the researchers involved have good depth on the subject matter.

Project weaknesses:

- There is no clear demonstration yet that the melt-spun carbon fibers will achieve the requisite strengths (greater than 600,000–700,000 pounds per square inch). Some parallel effort is needed to convert the filaments/tows, then measure their mechanical properties and relate them to the processing conditions and properties and microstructure of the precursor fibers.
- This project needs much more collaboration with various fields. It should make this project much more fruitful.
- There is little leveraged work presented outside of this project.
- This project needs to actually make fiber from the PAN to see if there are any unexpected implications of the methods used.
- The project should attempt to accelerate the making of a carbon fiber to assess if the melt-spun fibers are comparable to the wet-spun fibers, and if the modified plasticizers and additives affect the final fiber attributes. Additional connections and consulting from an industry partner would benefit the project.

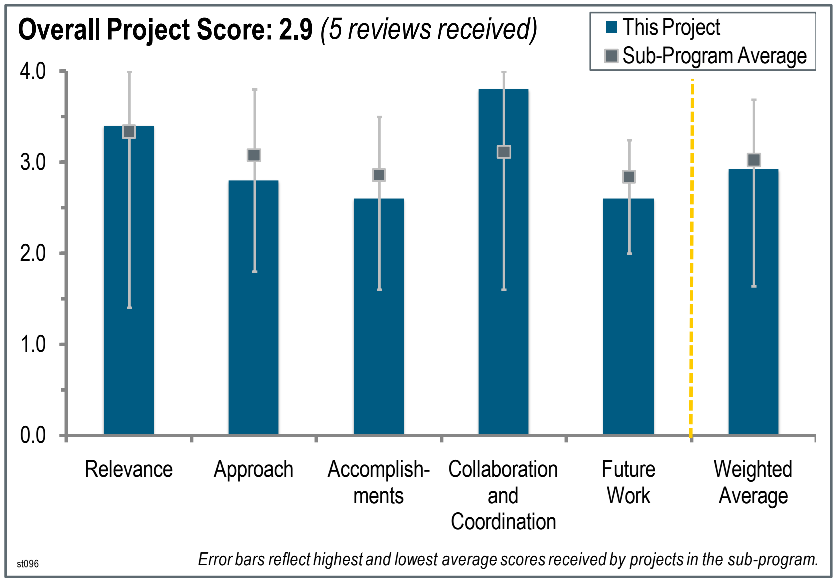
Recommendations for additions/deletions to project scope:

- The concept of this project looks fine; however, there is not enough collaboration and conversation with the stakeholders. The reflections from those people will very much inform further progress of this project. It is also recommended to collaborate with carbon manufacturers that can request the properties of the precursor needed for carbon fibers for onboard application.
- It will be beneficial to the commercialization of the process if the PI can get the industrial partner involvement at a very early stage.
- The team should make carbon fiber from the PAN a regular part of the program conduct.
- With the current knowledge of the process, a confirmation of the cost analysis should be conducted. Also, an industry partner could be included to evaluate the cost analysis assumptions.

Project # ST-096: Analysis of H_2 Storage Needs for Early Market Non-Motive Fuel Cell Applications

Lennie Klebanoff; Sandia National Laboratories

Brief Summary of Project:



The U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program is including in the scope of its Hydrogen Storage sub-program early market uses of fuel cells in non-motive applications, including construction equipment, telecommunications backup, portable power, and airport ground support equipment. DOE wants to understand the hydrogen storage performance gaps that hinder fuel cell use in these pieces of equipment. This project will use workshops to gather data from end users and technical experts and compare the energy storage performance demanded by the user with the current state of hydrogen storage technology while identifying any performance gaps.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.4** for its relevance to DOE objectives.

- This project focuses on storage system requirements for early market applications. The Program is emphasizing the introduction of fuel cell systems in early markets as a means of demonstrating the feasibility of this technology. This project is directed toward identifying and defining storage needs in the early market environment, and is very relevant.
- It is very important to identify the needs of the market rather than simply evaluate the capability of the new technology and then modify the requirements to meet that capability.
- Early market uses of fuel cells in non-motive applications are important. They relate to construction equipment, telecommunications backup, portable power, and airport ground support equipment including the understanding of the hydrogen storage performance gaps that hinder fuel cell use in these pieces of equipment.
- The Program includes early market non-motive fuel cell applications. These applications may have their own specific hydrogen storage needs. Understanding these needs and developing any storage technology needed will be important to the successful use of fuel cells in these applications.

Question 2: Approach to performing the work

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

- The approach taken collects data on the types of non-motive, early market applications from the end-user perspective. The applications have been identified through a workshop composed of 22 end users and 9 technical experts. Data collected at the workshop has been analyzed.
- This approach is very focused on incorporating end users into the process.
- The end-user workshop at Sandia National Laboratories (SNL) Livermore Valley Open Campus (LVOC) in February 2011 was good, but was limited to the specific group attending. Use of the Kano model, a way to characterize customer satisfaction, is unique in that it distinguishes between required requirements, those that are linearly satisfied, and “wow” characteristics.

- The project plan only includes the one workshop held with end-user stakeholders and storage experts and a questionnaire for these people to gather information. Working with these stakeholders is a good approach. It was stated that there would be follow-up conversations with various end users to further elucidate their storage needs. Additional focused follow-up workshops would likely yield valuable added information. The discussion and results from the February 2011 workshop held at SNL LVOC makes it seem that the workshop was more focused on identifying and defining non-motive fuel cell markets rather than focusing in on the important details of the key storage system needs for these markets. The use of the Kano model is interesting, but may be resulting in more effort than is readily needed for this project.
- While the project goal is to analyze the hydrogen storage needs for non-motive applications, the approach only addresses storage barriers for a limited set of these applications. The project is confined to a limited sector of non-motive applications and ignores other potential markets, such as portable power systems with average power levels below two kilowatts. The principal investigator (PI) stated that the categories chosen were predetermined from a Battelle report from about 10 years earlier, so this may have limited the flexibility with applications.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- The progress to date appears to be reasonable, with approximately one-half of the project schedule executed.
- The team has completed meetings and surveys and is in the process of evaluating the data.
- This project has made modest progress in overcoming barriers, though the rate of progress has been slow.
- The activities within this project are moving along at a reasonable pace. The information gathered so far and presented appears very general in nature. It is as much about the markets and fuel cell needs as it is about the storage needs for these markets. There are few to no details about the specific requirements for the storage systems. It was stated that the questionnaire and follow-up conversations with the end users will provide specific and more detailed information on the storage needs for these markets.
- In the short time available, the project has produced meaningful results within the limitations of the predetermined application choices. This reviewer would like to have seen more of the results that directly relate to the needs and gaps in hydrogen storage for the applications studied. For the most part, almost all of the conclusions shown in the presentation for user requirements have been understood for several years, or could have been derived from a preliminary study prior to the workshops and Kano studies. The reviewer asks whether there are other, non-reported findings from the study that are new and revealing of the needs of this set of power-system users.

Question 4: Collaboration and coordination with other institutions

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

- The team has done a very good job of integrating end users with technical experts.
- The collaborations and coordination with other institutions is good, as it helps with increasing efficiency and producing a complete product for DOE.
- There is excellent collaboration with the National Renewable Energy Laboratory (NREL), which is running a very similar project on motive, early hydrogen market storage needs. Information is being gathered from end users and storage experts.
- Collaboration among the partners appears to have been well done. Another important point is that the PI stated that the researchers are talking directly with the end users as well as using the Kano analysis to refine their database.
- There was some collaboration with other national laboratories and workshop participants.

Question 5: Proposed future work

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

- The workshop provided a good start for gathering information from both end users and technical experts, but future information gathering should be open to a wider audience.

- The plan to complete this project is adequate, but it does not appear to include enough effort on gathering more detailed and specific information about the storage needs and performance requirements for these non-motive, early hydrogen markets.
- The proposed future work was described through August, including the final report submission. The project goes through September, and this reviewer wonders why it is stopping a month early.
- The team will need to simplify the data into a straightforward, useful format that can be used to evaluate the applicability of hydrogen storage in the application and identify research needs.

Project strengths:

- The data analysis methodology from NREL is a strength.
- This project has active collaboration with NREL and the Pacific Northwest National Laboratory.
- Holding a workshop with end-user stakeholders and storage experts as well as offering a questionnaire to gather information is a good approach.
- It is apparent this is a very well organized team.

Project weaknesses:

- This project needs more data input from potential end users.
- The information gathering is limited to a particular audience.
- The discussion and results of the workshop held at SNL in February 2011 make it seem that this workshop was more focused on identifying and defining non-motive fuel cell markets rather than focusing in on the important details of the key storage system needs for these markets. Much more detailed information on the storage systems' requirements needs to be gathered.
- This project is a little shortsighted on the applications that may be meaningful for the commercialization of hydrogen and fuel cell systems. The duration of the project was short; a continuation may be beneficial.

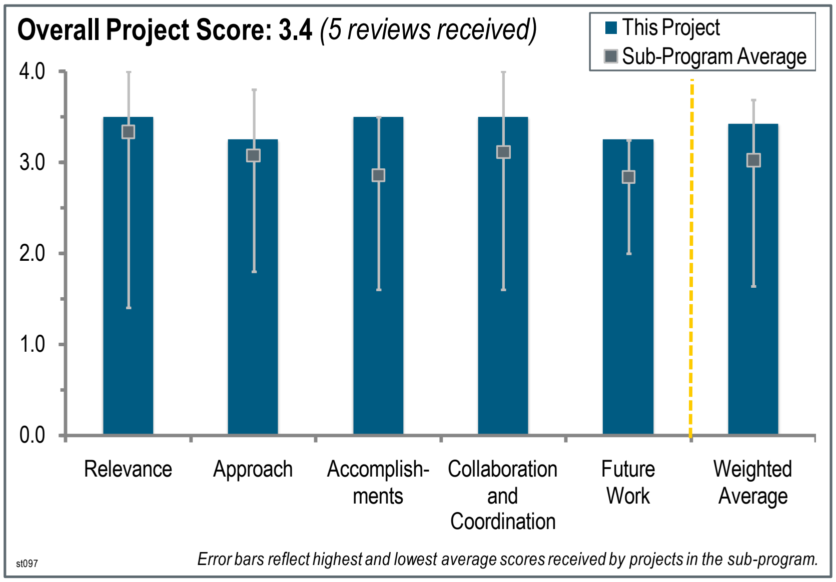
Recommendations for additions/deletions to project scope:

- More contact and input from potential end users would be helpful to build confidence in project findings. Collaborations with end-user organizations such as the International Facility Managers Association would be helpful to gain a broader base of end-user input.
- It would be useful to evaluate the performance of the current fuel and energy storage technology for each application. This would be beneficial in identifying the areas that hydrogen storage might make its earliest integration (technology pull rather than technology push).
- Much more detailed information on the storage systems' requirements needs to be gathered.
- This project should expand its field of applications and base expansions on the markets that may not be popular to market analysts, but that have growth that could potentially outpace those in this study or those favored by analysts (innovators' dilemma).

Project # ST-097: Analysis of Storage Needs for Early Motive Fuel Cell Markets

Jennifer Kurtz; National Renewable Energy Laboratory

Brief Summary of Project:



The overall objective for this project is to identify the needs of onboard hydrogen storage and the gaps in current hydrogen storage technologies as they relate to those needs in early fuel cell motive markets, while providing information to focus research and development efforts in hydrogen storage technologies that can accelerate market adoption. Objectives are to: (1) target key early fuel cell motive markets such as material handling equipment, ground support equipment, public transit, and unmanned vehicles; (2) work with end users in the key markets to understand the performance needs related to onboard energy storage; and (3) work with hydrogen storage experts and manufacturers to understand current technology capabilities and how that compares with the market performance needs.

Question 1: Relevance to overall U.S. Department of Energy objectives

This project was rated **3.5** for its relevance to U.S. Department of Energy (DOE) objectives.

- This project attempts to gather input from potential end users on storage needs for early motive fuel cell markets. The DOE Hydrogen and Fuel Cells Program wants to facilitate the early market introduction of fuel cell applications. Identifying and defining the storage requirements for these early markets is very relevant to current DOE goals and objectives.
- It is important to identify the storage needs of each application to evaluate the applicability of the hydrogen storage to the application.
- The project addresses the energy storage performance needs for early fuel cell motive markets, which is important to DOE's overall objectives.
- The Program includes early market motive fuel cell applications. These applications may have their own specific hydrogen storage needs. Understanding these and developing any storage technology needed would be important to the successful use of fuel cells in these applications.

Question 2: Approach to performing the work

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

- The approach based on end-user-focused workshops is appropriate for this project. Gathering pertinent inputs at these workshops and using standardized data analysis methodologies is valid and an essential element of the project.
- The meetings held with various groups—including end users, experts, and novices—will give an important range of data.
- The approach of working with end users, manufacturers, and experts to gather information through workshops and questionnaires for an analysis to identify the motive market's specific performance needs and current hydrogen storage technology gaps is important.

- This project has identified the key markets up front so the researchers can target these areas specifically. The researchers worked directly with end users and other stakeholders through three workshops and an electronic questionnaire. The workshops and questionnaire get into the details needed to define any gaps that need to be addressed through research efforts. The Kano approach for the questionnaire is interesting, but it may be overkill for this effort.

Question 3: Accomplishments and progress towards overall project and DOE goals

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

- Progress to date has been exceptional, with three workshops conducted and the input from end users attending these workshops analyzed. The storage-need findings to date appear to be logical and consistent.
- The question of identifying performance needs produced more discussion than the question of what areas can be improved. The suggestion to involve more end users is a good one.
- The project is adhering to the original schedule and making good progress. The workshops have been held with useful results, and the electronic questionnaire has been issued with results coming in now.

Question 4: Collaboration and coordination with other institutions

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

- Collaborations with two other national laboratories are cited. Partnering with end-user trade organizations would be useful.
- The team has incorporated a diverse group of participants into the study.
- Collaborations with the Sandia National Laboratories and the Pacific Northwest National Laboratory (PNNL) are good to achieve DOE’s objectives.
- There is good collaboration with the sister project on non-motive early markets and PNNL. There is excellent collaboration with end users and other stakeholders through the workshops.

Question 5: Proposed future work

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

- The future work plan is excellent. It includes gathering more information and details about the storage needs of these early motive fuel cell markets, gathering information on the availabilities of current hydrogen storage technologies, and performing a gap analysis.
- The future work planned to complete the project seems to be reasonable. An additional workshop is planned and should provide additional end-user input.
- The key to achieving a successful study will be to simplify the data into a useful format that will identify the applicability of hydrogen storage technology to the application.
- The final report addressing onboard storage needs for early fuel cell motive markets and the corresponding hydrogen storage gaps related to key market summaries, including potential improvements for hydrogen storage systems, will be helpful.

Project strengths:

- The data analysis methodology and the project plan and approach are strengths of this project.
- The project findings will aid DOE in focusing on hydrogen storage research and development efforts for early motive fuel cell markets.
- This project has identified the key markets up front so the researchers can target these areas specifically. The researchers are working directly with end users and other stakeholders through two workshops and an electronic questionnaire. The workshops are getting into the details needed to define any gaps that need to be addressed through research efforts. There is excellent collaboration with end users and other stakeholders through the two workshops. The future work plan is excellent. It includes gathering still more information and details about the storage needs of these early motive fuel cell markets, gathering information on the availabilities of current hydrogen storage technologies, and performing a gap analysis.

Project weaknesses:

- This project could involve more end users.

Recommendations for additions/deletions to project scope:

- It is strongly recommend that the project have the final planned workshop, as additional end-user input would be very useful and should broaden the data.
- The performance of the existing fuel- and energy-storage mechanism needs to be quantified. For example, diesel fuel storage on buses might meet all of the storage requirements (range, weight, cost, etc.), but battery technology might fall short in forklift applications (limited range). This would identify applications that need (technology pull) hydrogen storage rather than applications where hydrogen storage is a “good” idea (technology push).