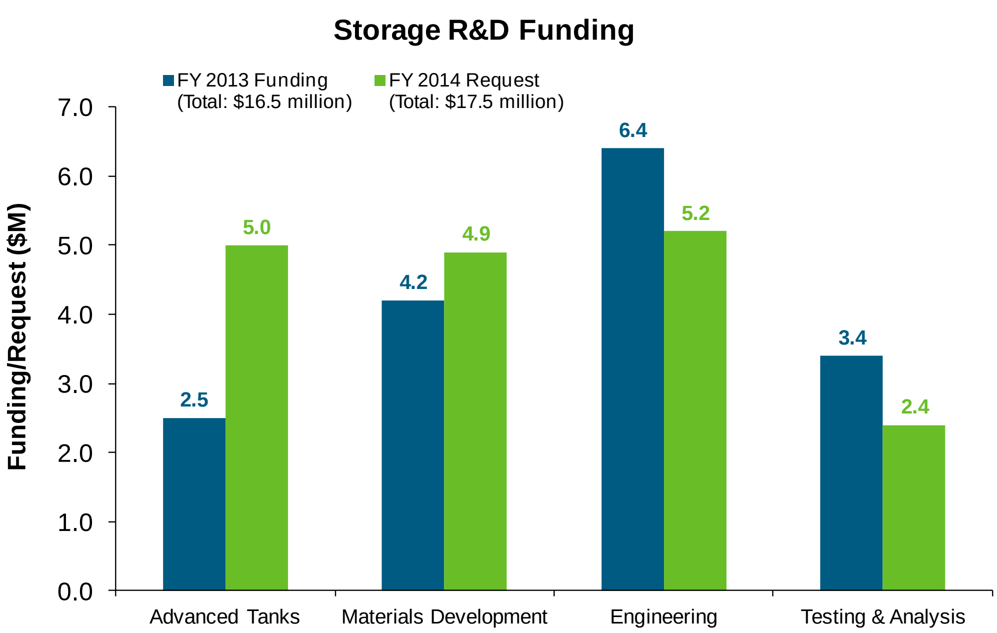
2013 — Hydrogen Storage
Summary of Annual Merit Review of the Hydrogen Storage Program

Summary of Reviewer Comments on the Hydrogen Storage Program:

In fiscal year (FY) 2013, the Hydrogen Storage program portfolio focused on system engineering for onboard transportation applications, with continued efforts ongoing for materials-based research and development (R&D) and physical storage options for near-term deployments. Reviewers commended the program's use of valuable results from the Hydrogen Storage Engineering Center of Excellence (HSECoE) to help direct and focus materials development. Reviewers felt that the program's efforts to expand the research portfolio to include non-automotive applications, such as material handling equipment, portable power, and stationary applications, were good. Reviewers remarked that the program was underfunded, though they also stated that the current portfolio does a good job of covering key areas. With additional funds, reviewers noted the potential benefits of more materials discovery research efforts. Overall, reviewers commented that the program is very well managed and should continue to focus on meeting all onboard automotive targets and encouraging the development of hydrogen storage for non-automotive applications.

Hydrogen Storage Funding by Technology:

The chart below illustrates the appropriated funding planned in FY 2013 and the FY 2014 request for each major activity. The program received $16.5 million in funding in FY 2013, and it has a budget request of $17.5 million for FY 2014. The HSECoE continues to be a major activity for the program with additional efforts aimed at lowering the cost of compressed hydrogen storage. Work on hydrogen storage materials development is also an important part of the portfolio that will continue to be an area of focus, especially as more information regarding material-level property requirements is derived from the system engineering efforts. Additionally, there is a planned increased emphasis on early market storage applications in FY 2014.



Majority of Reviewer Comments and Recommendations:

The Hydrogen Storage portfolio was represented by 27 oral and 11 poster presentations in FY 2013. A total of 28 projects—via 24 oral and 4 poster presentations—were reviewed. In general, the reviewers' scores for the storage projects were good, with scores of 3.6, 3.1, and 2.2 for the highest, average, and lowest scores, respectively.

Advanced Tanks: Four projects on advanced tanks were reviewed, with a high score of 3.4, a low score of 2.7, and an average score of 3.1. Overall, reviewers felt that the work being done is addressing key areas and that significant progress is being made. Reviewers felt that the projects are well organized and that efforts to improve carbon fiber precursor materials and composite-overwrap properties were appropriate because the carbon fiber composite is the largest contributor to the overall tank costs. Reviewers thought that strong progress was made in the projects but noted that some projects could be aided through additional collaboration. Reviewers also suggested inclusion of clear cost assessments for the projects.

Materials Development: Eleven materials-based hydrogen storage projects were reviewed, with a high score of 3.4, a low score of 2.2, and an average score of 2.8. Generally, reviewers commended the materials development projects for integrating computational and experimental efforts. The reviewers appreciated the wide range of material types being investigated, including metal hydrides, adsorbents, chemical hydrogen storage materials, liquid carriers, and nano-confined liquids, and found continued investigation of all material classes to be relevant to the program. However, they also commented that many of the materials currently under investigation would not be able to meet the full set of U.S. Department of Energy (DOE) targets for automotive onboard storage of hydrogen. The reviewers also commented that negative results are of value to the community, including when materials and synthesis approaches are not successful, because capturing that information for future reference is valuable. Materials projects will continue in FY 2014, subject to appropriations, with an emphasis on a stronger link and feedback route between the experimental and theoretical efforts and more emphasis placed on meeting projected material-level property requirements to meet the system-level targets.

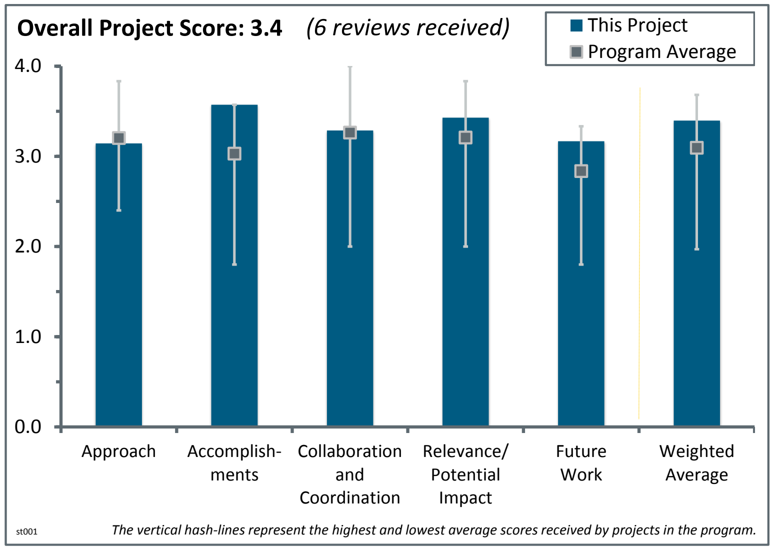
Engineering: Ten projects were reviewed on hydrogen storage engineering, with a high score of 3.6, a low score of 3.0, and an average score of 3.3. Reviewers stated that the HSECoE made significant progress in FY 2014 and featured strong coordination and clear collaboration among the partners. They also commented on the importance of systems engineering efforts, especially in determining the material-level properties required to achieve the Hydrogen and Fuel Cells Program storage targets. The reviewers commented favorably on the development and use of integrated models on projecting system performance. In general, the reviewers considered the projects of individual HSECoE partners to be well thought out and feature expert personnel who execute clear plans. The reviewers considered the sorbent system efforts to be making good progress and to be well designed. Similarly for the chemical hydrogen systems, the reviewers favorably commented on the progress of reactor design, gas cleanup, and balance of plant work. However, for both system types, the reviewers were concerned with the applicability of the efforts to the broad class of materials because none of the surrogate materials being tested are able to satisfy the full set of DOE onboard storage targets. Overall, reviewers thought the HSECoE and its partners were making good progress in evaluating materials-based storage systems and making decisions to meet DOE performance targets.

Testing and Analysis: Three projects related to testing and analysis were reviewed, with a high score of 3.6, a low score of 3.3, and an average score of 3.4. Reviewers stated that these projects are critical to the program because these analyses help develop targets and guide research to maximize impact. Reviewers felt projects in this area used a robust and comprehensive approach, and that significant progress has been made in cost reduction through carbon fiber and compressed tank cost estimates. Reviewers commended the excellent collaboration and cooperation displayed in each project to ensure coordinated assumptions and efforts in the community. Reviewers thought that validation of models and analysis was worthwhile and suggested prioritizing carbon fiber analysis over metal hydride work in the future. Reviewers thought the Best Practice manual was extremely useful for the community and very well done, and that good progress has been made on thermal and mechanical properties. Overall, reviewers noted that a strong team performed thorough analyses and emphasized the importance of these projects in improving the quality of research in the program and providing clear insight to guide future research.

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

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project:



This project performs independent analysis to evaluate the onboard and off-board performance of materials and systems for hydrogen storage. Results are provided to material developers for assessment against performance targets and to help them focus on areas requiring improvement. Inputs are provided for independent analysis of the costs of onboard systems. Interface issues and opportunities and data needs for technology development are identified. The project develops and validates physical, thermodynamic, and kinetic models of processes in physical and material-based systems to address performance targets including capacities, rates, and efficiencies.

Question 1: Approach to performing the work

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

- The project employs a multifaceted approach, which is well suited to the variety of technologies being addressed.
- The approach taken for both of the tasks reviewed appears to be reasonable, and the work appears to be well integrated.
- The work is well coordinated with the efforts of the Hydrogen Storage Engineering Center of Excellence (HSECoE), although there are some redundancies. The U.S. Department of Energy (DOE) needs to decide going forward who should take the lead on systems modeling—Argonne National Laboratory (ANL) or the HSECoE. The principal investigator (PI), however, is a natural fit for these tasks. The focus is not necessarily to achieve the overall U.S. DRIVE Partnership targets, but rather to understand the systems engineering trade-offs/trends required to package materials into a system. This provides guidance to material developers on what materials characteristics to consider.
- This project features a very nice and comprehensive approach that looks at very different systems both for near-term (compressed gas storage) and long-term (metal hydrides) usage for automobile applications (as well as some stationary applications). Simulations on the stress profile ought to be verified by experiments. So far none have been conducted; however, they are important and must be done in this or a follow-up project. Because mobile applications are currently a long-term option for usage of metal hydrides, some suggestions ought to be made about possibilities for using the gained knowledge in the meantime. Perhaps there are possible spin-offs?
- It is not clear which approach was chosen to address the barrier "life cycle assessment." The project takes a good approach to combine different fiber qualities. It would be desirable to have a matrix or an overview to show the correlations between barrier, approach, and accomplishment.
- Barriers identified are realistic targets for improvement and the approach directly addresses them. However, the scope of the presentation is extensive to the point of perhaps being too broad. It is hard to take in comparison of these different technologies given that they are really at different readiness levels. The ranking reflects an inability to get a complete view of the "big" picture.
- The approach of the project to conduct technical modeling of various storage systems is fine, but validation of the assumptions or results is lacking. It would be useful to include further background regarding the sources of certain assumptions and comparison of model results with physical testing or values. For

example, the tank and system weight projections could be compared to actual systems. Also, it would benefit the industry to have an explanation of the reasons for changes in the model projections from previous years.

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

This project was rated **3.6** for its accomplishments and progress.

- The progress appears to be excellent.
- The project's progress includes an improved assessment of the compressed tank carbon fiber (CF) utilization. The effort in reverse engineering the metal hydride material target values was also a valued accomplishment.
- Progress is excellent relative to the HSECoE targets, which are lower than the overall DOE targets. The systems modeled will not achieve DOE targets but are in line with the HSECoE targets. The modeling highlights how much improvement in particular metrics are required to achieve DOE targets.
- The project features a very good, broad approach, considering physical and chemical hydrogen storage and different types of materials. Researchers have achieved very good results concerning cost reduction and needs for materials.
- Researchers have shown some possible combinations of how to reduce the amount of high-quality CF. However, there is no direct correlation to the DOE targets.
- The project has done thorough work in the areas of focus to date. The integration approach for the resin end cap could be more clearly spelled out. Sensitivities to fiber winding model assumptions should be examined. The project should also examine whether the candidate list of metal hydride materials changes if the fueling time assumption is relaxed somewhat.
- Good progress was shown for both the physical storage and the metal hydride tasks, but no or very little progress was described for the sorbent and off-board regeneration tasks. Also, the summary of work on slide 5 states that a comparison of hydrogen storage in metal hydrides for this project would be made with results and methodology from the HSECoE; however, it would have been good if some of those comparisons were discussed in more detail in the presentation.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration and cooperation seem to be very reasonable.
- It seems that all relevant partners are included.
- The project supports and coordinates well with industry, engineering centers, universities, and national laboratories.
- This project's work complements the HSECoE effort and has the appropriate mix of industry, academia, and national laboratories.
- It is clear collaboration is occurring between the right parties, but it is hard to discern if it is the best collaboration possible.
- Collaboration with the HSECoE for the metal hydride task and with Pacific Northwest National Laboratory, Ford Motor Company, and Lincoln for the compressed hydrogen task was good, but the collaborations on the unreported tasks were difficult to evaluate at this time.
- ANL has a good level of collaboration with others in hydrogen storage research. ANL should be encouraged to coordinate its assumptions and effort with the HSECoE to avoid duplication of work. In particular, the metal hydride target material properties were already evaluated by the HSECoE. It would have been useful to compare the results and provide a consensus table of target values for the metal hydride material.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The project's contributions to the two completed tasks are well aligned with the current Fuel Cell Technologies Office objectives.
- The project provides needed analysis input to develop targets for other Hydrogen Storage program projects.
- This project shows very high relevance and potential impact by looking at near-term progress (compressed gas) as well as long-term potential (metal hydrides).
- Because CF costs are the main part of the total system cost, the results of this project are very important. However, the proposed future work on metal hydrides should have a lower priority compared to CF.
- The achievements, if incorporated into products by industry, will advance the capability of the systems.
- The project has relevance as an independent system analysis of various hydrogen storage concepts. The effort is very similar to the HSECoE effort, but it does not include the physical confirmation of the modeling that is included in the HSECoE analysis. The potential impact could be further improved by highlighting areas of uncertainty in the models that should be validated or emphasizing the key research needs to further advance the hydrogen storage system research.

Question 5: Proposed future work

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

- The future work plan looks good, especially in the efforts to conduct validation with physical confirmation testing and complete reverse engineering for various material-based hydrogen storage systems.
- Validation of the models and results is exactly what is needed and is planned.
- The proposed validation of CF simulation is very important. The metal hydride effort should have a lower priority.
- Additional material targets are needed. Validation of CF designs may require more than coupon testing—possibly standards-based qualification testing.
- The PI should provide a trade-off analysis of how to accommodate for buffer hydrogen volume (required for system start-up) to determine whether a separate buffer tank be included in the system or if extra volume should be added to the existing sorbent vessel. A cost and volume trade-off analysis would be beneficial at the next review.
- The proposed future work logically derives from the work just reported. However, at some point the storage capabilities of each particular technology will face comparison and there will be a need to select the technologies that most realistically meet market requirements. This focus is not addressed here, nor was it indicated in the project scope.
- The researcher should not continue the metal hydride task for higher temperature metal hydrides, especially for automotive applications. Even for non-automotive applications, the researcher should spend more effort on the sorbent and the chemical hydride regeneration tasks.

Project strengths:

- A strength of this project is its broad approach.
- The work on physical storage is straightforward and seems to be making good progress.
- This project featured excellent coordination with industry and academic partners to provide realistic system performance and data.
- This is a broad-based project that is providing important data to other projects within the Hydrogen Storage program.
- The PI and ANL have extensive background in hydrogen storage and capability in modeling.
- A strength of this project is its focus on the main cost driver (CF) to reduce the amount of high-quality CF.
- The PI has a good background and experience and expertise in this area. The work appears to be thorough and sound. The PI has demonstrated a good ability to partner with other PIs during his analyses.

Project weaknesses:

- Experimental verification is required.
- The PI has made numerous presentations but should strive for more journal publications.
- The project could improve by providing validation of results and confirmation/progress in the assumptions.
- While the work on metal hydrides, sorbents, and off-board regeneration is clearly making progress, the presenter did not spend enough time comparing the capabilities of the different technologies.

Recommendations for additions/deletions to project scope:

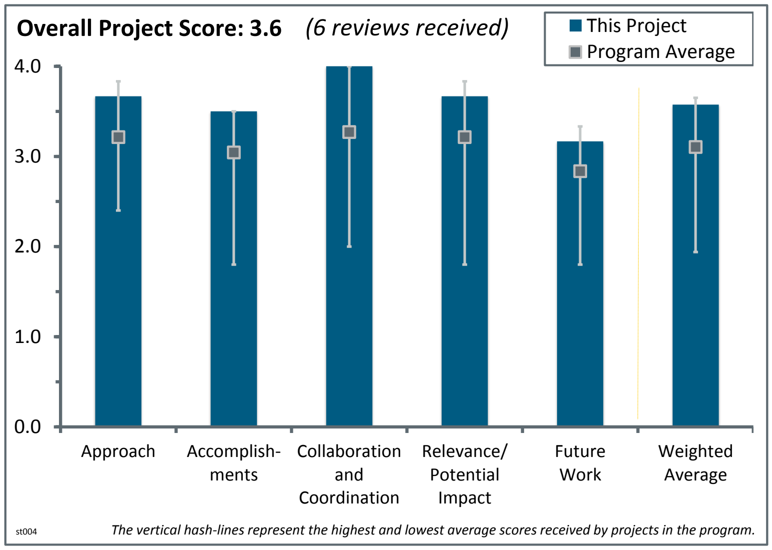
- The skill set and model should be adapted to model compressed natural gas sorbent-based systems.
- The project team should clearly articulate which work package is for automotive and which is for non-automotive applications.
- The project should include recommendations for future improvements to hydrogen storage systems by conducting sensitivity analysis with the models.
- The project team should separate the metal hydrides and sorbent efforts from the physical storage. Then it could consider allowing another project element (presenter) to address cost effectiveness.
- The work on the metal hydride tanks is an important task because—even if targets have not been met so far—metal hydrides are the only storage option that, in the long term, offers a possibility to overcome present restrictions concerning weight, volume, and cost. Nevertheless, at present for automobile applications, they offer only a long-term perspective. Therefore, it is required that the scientists also give some ideas about possible short-term applications that could allow for a return of investment for the taxpayer in the medium term.

Project # ST-004: Hydrogen Storage Engineering Center of Excellence

Don Anton; Savannah River National Laboratory

Brief Summary of Project:

This project uses systems engineering concepts to design innovative, material-based hydrogen storage system architectures and to build and evaluate subscale prototype systems to assess those architectures to improve both component design and predictive capability. The project will develop and validate models for measuring fuel cycle efficiency. Data from these models will be compiled to define required materials properties to meet technical performance and cost targets.



Question 1: Approach to performing the work

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

- This project has an outstanding and comprehensive approach that includes several different storage alternatives and compares them in one project. It is very good.
- The Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center) approach has proven much more effective than having individual partners attempt these tasks. The task of designing novel systems based on hydrogen storage systems requires knowledge that was previously unavailable. The tasks require the guidance of industry end users to determine system requirements, the resources and expertise of national laboratories, and the materials synthesis expertise and knowledge of academia. The HSECoE targets are generally lower than the overall U.S. Department of Energy (DOE) targets. These targets were set based on the knowledge that storage materials available today cannot yield systems that would achieve the targets. The targets set are challenging and are intended to provide an understanding of what further characteristics in storage materials must be considered to ensure efficient system design.
- This is a comprehensively well-organized project that is focused on the critical technical barriers to achieving a broadly implemented hydrogen-fuel-cell-based passenger vehicle market in the United States. The project matrix structure presented in slide 6 of the Savannah River National Laboratory (SRNL) presentation illustrates the well-integrated nature of this highly effective collaboration in a clear and concise manner. The spider charts provide a fully transparent map of progress over time. In this regard, the modified spider charts, showing year-to-year and/or phase-to-phase progress, are a valuable addition to the presentation format.
- The principal investigator (PI) has created a credible organization with well-defined teams and division of responsibilities. The scope of work for Phases I, II, and III is clearly laid out, as are the Phase II go/no-go milestones. The Center has made a no-go decision on metal hydride systems and is pursuing adsorbent and chemical hydride system options in Phase II. Although a Phase III go/no-go determination was to be made by March 31, 2013, the PI did not discuss what was decided and how the decision was made.
- The Center has several approach variants to two general hydrogen storage options—chemical hydrides and cryo-adsorbents. The sub-projects have analytically and experimentally studied the storage materials, the system designs, and some of the balance of plant (BOP) components. The Center has done well in developing and leading this approach.
- A sensible and comprehensive technical approach comprising modeling, system concept development and testing, and component integration has been adopted for the Phase II effort. Surrogate adsorbent metal-organic-framework-5 (MOF-5) and chemical hydrogen storage materials (ammonia borane [AB] and alane) have been selected for engineering prototype development. It seems reasonable that engineering

development based on MOF-5 will be extendable to future adsorbent systems. Also, given the lack of an ideal chemical hydrogen storage material, the development of prototypes based on both endothermic and exothermic systems is appropriate and prudent. However, the numerous problems faced by the AB system (not the least being the lack of a cost-effective regeneration pathway and the complexity of the overall system design) seem to make the adoption of that material highly problematic. The approach should include a more tightly focused effort on engineering development with the alane system.

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

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

- The accomplishments and progress in the different technologies are amazing and convincing. They are very good.
- Tremendous progress has been made in the last year. In particular, for the sorbent systems, many of the results are now available regarding the relationship between materials, packing, heat, and gas flow. These were the Center's original goals.
- Progress has been made in all aspects of the project during the past year. All three storage types (compressed gas, chemical hydrogen storage, and sorbent) have been brought to a higher level of detail and performance. Unmet gravimetric and volumetric storage targets, as well as cost targets, still prevail. In truth, the spider charts reflect only incremental advances toward targets in most cases. Considering the level and quality of the experimentation and analysis going into the project as a whole, this incrementalism suggests that perhaps the project as a whole is nearing the limits of what is possible. The continued expansion/validation of analysis and modeling capability on the website is resulting in the establishment of a valuable resource to the DOE Hydrogen and Fuel Cells Program that must be maintained to accommodate future advances in the state of the art for hydrogen storage and in-vehicle fuel treatment. Performance analyses show that, at present, there exists the possibility of getting close to a vehicle with a 300-mile range with what they expect to have by the end of Phase III.
- Good progress has been made in 2012/2013, especially in two areas: (1) chemical hydrogen reactor development, reactant delivery, and BOP gas purification; and (2) media system engineering, including a down-select of workable solutions for optimized heat exchange and thermal conductivity. The technical effort obviously has been tailored to transition to Phase III implementation. The selection of MOF-5, as well as AB and alane as surrogate material systems, allowed solid progress to be made on the development of a framework for adsorbent and chemical hydrogen storage systems. However, it will be essential for the Center to take a much more critical look at the overall efficacy of AB and its derivatives in a practical vehicular storage system. The evolution of the chemical hydrogen storage AB prototype engineering system design to ever-increasing complexity is a disconcerting trend.
- The HSECoE has done a good job in moving chemical and adsorbent hydrogen storage systems forward. For the overall Center cost of approximately $500,000/month over 5 years, the progress appears to have been somewhat slow. There are some valuable accomplishments, but it is not completely certain that all of the remaining barriers will be sufficiently addressed for the chemical or adsorbent storage approaches to be fully competitive for light-duty fuel cell electric vehicles by the end of the project. The reduction in operating pressure and the move to an aluminum Type I tank for the MOF-5 material was very helpful in reducing system cost. The addition of usable models on the website can be valuable in opening the opportunity for others to contribute to improved hydrogen storage systems. Hopefully the site will be able to be maintained following the end of the Center
- The Center has done good work in developing engineering methods of handling and dealing with AB as a hydrogen carrier. AB in BmimCl has been abandoned in favor of AB slurry using the SafeHydrogen approach of using silicon oil. The Pacific Northwest National Laboratory (PNNL) results seem to indicate that 45 wt.% AB (7 wt.% hydrogen) and spent AB slurry are stable after sonication, but the kinetics are very slow at 120°C in that more than 100 minutes that are needed to release >1.5 hydrogen equivalents. Los Alamos National Laboratory has developed an auger reactor for slurry dehydrogenation, but 280°C is needed for 100% conversion in 6.8 minutes. It is not clear if this holdup time is excessive and how it impacts start-up, shutdown, and transient response. United Technologies Research Center (UTRC) has developed a gas-liquid separator that meets the volume but not the weight target. UTRC has also

successfully tested ammonia and borazine filters. PNNL has tested a volume displacement tank for storing AB in silicon oil. All in all, good progress has been made in developing the system components. Further work is needed to increase the solid loading and improve the hydrogen purification system. The problem all along has been that the off-board efficiency of AB regeneration is unacceptably low (<30%) and the cost is prohibitively high (>$50/kg). It is difficult to see how the AB system can pass the Phase III go/no-go decision.

- The Center has done good work in developing engineering data and components for cryogenic hydrogen storage in adsorbents. The Ford Motor Company/University of Michigan/BASF team has collected useful data on the effect of MOF-5 densification on hydrogen uptake and permeability but has not been successful in identifying a "compact" structure that meets all of the requirements. The Center has confirmed that Type IV tanks are not suitable for service below the polymer glass transition temperature. The Center has selected Type I rather than Type III tanks for cost savings and manufacturability at the expense of additional weight. The effort possibly could have been avoided if a proper literature review was made. Perhaps better planning could have also been done before embarking on the cryo burst test facility and exhausting the funds. It appears that the Jet Propulsion Laboratory effort to find alternate cryo-insulation materials has not been successful because the Center is using multilayer vacuum insulation (MLVI) with Dacron spacers. The Center continues parallel development of modular adsorption tank insert (MATI) and internal flow (HEX) options for heat exchange. In summary, the Center has done well in addressing the material behavior and component design issues and in developing models for system performance. However, the projected well-to-plant efficiency for hydrogen storage at 80 K is very low and the fuel cost will be high. It will be interesting to see how these factor into the Center's go/no-go decision for hydrogen storage in cryo sorbents.

Question 3: Collaboration and coordination with other institutions

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

- This is the best balanced center that the Hydrogen Storage program has had. It has the right level of collaboration from industry, academia, and laboratories. Guidance from the U.S. DRIVE Hydrogen Storage Tech Team, e.g., from Ford Motor Company on sorbents and General Motors on chemical hydrogen storage materials, has helped to provide realistic goals and targets and critical automotive feedback for the Center. The laboratories provide the capability to build, analyze, and test these systems that the original equipment manufacturers do not have resources to conduct. Materials development and characterization is being conducted by the academic partners.
- The project has a strong team of partners from national laboratories, academia, and industry. The PI appears to have done well in coordinating the contributions of the team members. There was little evidence of collaborations from people and institutions outside the team.
- It is amazing how well these different and excellent people and research groups collaborate and how well such a big project is coordinated by the PI. He succeeded to form an excellent working team of outstanding researchers doing a great job. The project is internationally well recognized and has an enormous impact both nationally and internationally. Very good job!
- This project is replete with examples of closely coordinated interfacing of partners. All of the presentations reflected an attitude that the project has been very effectively led by SRNL. The project is well directed/supervised by SRNL at a very reasonable per annum management cost ($300,000 per year).
- This is a complex project comprising multiple technology thrusts with a large number of technical obstacles and challenges. Success depends strongly on close collaboration and careful oversight of complementary and synergistic activities. The PI and his management team have done an excellent job of coordinating the work and ensuring that the numerous cooperating partners are communicating effectively and are all contributing in a significant way to the overall effort. The robust communication channels that are operative in the Center have enhanced the synergy among partners and have created a means of effectively communicating to all collaborators the technical challenges that must be met to successfully deploy a working prototype system that meets DOE targets.
- The Center continues to coordinate all of the collaborators very well.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Hydrogen storage is the major hurdle for the implementation of a future hydrogen-based society. The relevance and potential impact of this outstanding and very well managed project for the Hydrogen and Fuel Cells Program, the United States, and the world is enormous.
- The project is addressing all of the critical aspects of the technology required to provide a fully functional hydrogen storage and in-vehicle fuel delivery system for a passenger vehicle (see slide 2 of the Anton presentation). The entire HSECoE project is really a materials-to-wheels activity that is showing steady progress toward the DOE Hydrogen and Fuel Cells Program goals and targets. All aspects of the HSECoE effort align with DOE RD&D objectives.
- The project directly supports the DOE hydrogen storage objectives, and the project team is doing a commendable job of addressing the daunting challenges to developing a practical engineering prototype that meets the DOE goals. The lack of material systems that satisfies all DOE targets is especially problematic because the project has been forced to create and implement prototype engineering solutions based on surrogate materials whose properties may or may not be representative of optimized storage media that may emerge in future work.
- It is very important for the Phase III experiments and their iterations to show whether storage materials or systems can meet the DOE storage goals. To date, the analysis and testing appear to be lagging in some areas to where the technical status of all of the project elements may not be sufficiently understood to determine the likelihood of achieving DOE goals.
- Understanding the systems implications of hydrogen storage serves a dual function: it promotes understanding of 1) what improvements are needed in the materials to allow for more efficient systems, and 2) the physical limitations of systems. This will help both materials developers and vehicle packaging experts to better understand the limits and capabilities of hydrogen storage systems.
- The objective of this project is to design innovative material-based hydrogen system architectures to meet DOE performance and cost targets. Even at the start, it was recognized that a storage system could not be engineered to overcome the limitations of the materials that are currently available. The hope is that the analysis and characterization methods and components developed in this project will be useful and relevant when new promising materials are discovered by others.

Question 5: Proposed future work

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

- The proposed future work is recommended and necessary, and it should be done as planned.
- This keynote presentation on the progress of the HSECoE contained a clear, concise overview of the future plans and future expectations for the Center. A no-cost extension to March 2015 is planned in order to allow completion of all essential testing. This seems reasonable and should be viewed as such by DOE's EERE.
- The Phase III plans look very aggressive, but all of the elements of the plans are important. It is difficult to see how a significant portion of the Center's plans can be accomplished by the end of the first quarter of fiscal year 2015.
- The PI presented Gantt charts and "Specific, Measureable, Attainable, Relevant, and Timely" (SMART) milestones for Phase III work. He considers the Phase III demonstration as critical to model validation. DOE and the HSECoE need to discuss whether this should be the main purpose of the final phase of this project.
- The focus on gas cleanup techniques should be deemphasized in favor of materials that do not produce side products that are this undesirable. Gas cleanup is very specific to the hydrogen storage material. Because these materials are not suitable for the ultimate goals, the PI should provide justification that future materials may have some of the same undesirable side products in order to justify further work on cleanup. Cleanup systems are difficult to tune so that they work in all automotive working conditions.

- Based on this overview presentation and the supplemental charts that were supplied, it was not completely convincing that a carefully developed plan that addresses critical technical problems has been proposed for the Phase III effort. A clear and unambiguous statement of obstacles, specific technical challenges, and risks (especially in the AB work) was not provided. It is difficult to fully discern what the project team believes are the most critical technical problems that must be addressed. At this stage of the project, a straightforward and compelling statement of the remaining problems, areas of technical risk, and mitigation strategies is needed in order to provide DOE and the reviewers with confidence that a Phase III effort will result in solid progress toward a system (or systems) that satisfies DOE goals.

Project strengths:

- This project has excellent management and collaborations and a well-defined approach. The Center Director should be commended for forming and managing a great team.
- This project features brilliant management and a brilliant consortium. The stronger focus on what really matters in the end—i.e., the cost—is very good.
- This project benefits greatly from a well-conceived and effectively implemented project management structure as well as the fact that it is superbly well staffed at all partnering institutions. The overview presentation covered the operational and performance aspects of the project in sufficient detail to give a clear picture of where the technology stands and what needs to be done to achieve a successful outcome.
- A highly qualified technical and management team is conducting work on this project. The team has expertise and background in all areas that impact the successful development of a practical storage system. The HSCoE has done a good job of down-selecting candidate material systems and engineering solutions that should provide a solid basis for final prototype system development.

Project weaknesses:

- There are no glaring weaknesses that need to be corrected. One observation is that, considering the overall budget, the HSECoE has not produced any landmark innovations. The activities are developmental rather than being research oriented. The Center builds on system concepts that existed before it was formed.
- This project grows stronger by the year. The intensity of the efforts of all participants is obvious. If in the end the final outcome is not overwhelming, it will not be for lack of dedicated/productive effort by the HSECoE participants. The principal weakness of the project from day one has been the fact that the original DOE/EERE hydrogen system storage capacity targets were never achievable in the first place. Back-of-the-envelope calculations (calculations any educated scientist could do) will show that (1) the currently chosen storage options are very near the limit of what is possible and (2) the “current” 2017 system target for capacity (gravimetric and volumetric combined) is not achievable at the presently stated values.
- Because of its exothermicity, researchers should look into measuring the spatial stability control to demonstrate the ability to confine the reaction within a specific linear region of the AB slurry reactor.
- The signature problem that may ultimately limit overall project success is that no single material that meets all of the DOE targets has been identified. Consequently, engineering systems based on sub-optimal materials are being developed. It is becoming increasingly apparent that the AB system has some severe limitations; a more concentrated effort on the alane system is needed. It is unfortunate that the presentation did not include the critical work that was most relevant to understanding the progress made on the alane system engineering development.

Recommendations for additions/deletions to project scope:

- This is a very successful and well run project that should not end in 2014. It should be extended because hydrogen storage will remain an important task in the future and further improvements are still required in costs, operation conditions, and density. This consortium has acquired a huge know-how in hydrogen storage technologies that is not found elsewhere. In the case of those technologies that cannot meet the gravimetric targets so far, the consortium should think about other possible applications (portable or stationary) or spin-offs of their research work. In the case of the metal hydrides, the project team should

also consider how much the costs can be reduced if, for example, used structural materials are recycled as hydrogen storage materials, because recycling is becoming a more important aspect in many industries.

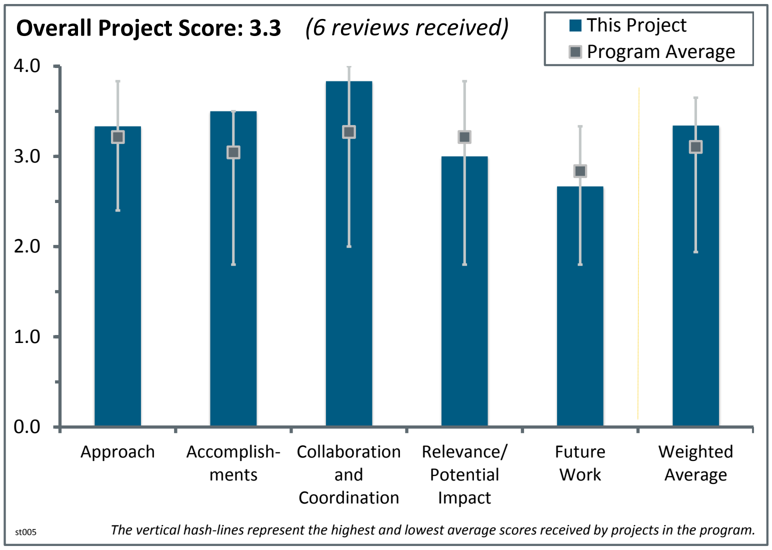
- As knowledge accumulates between the interactions of the materials and system design, the HSECoE should begin to provide more sensitivity analysis to understand where improvements can be achieved and how much is required in particular metrics to achieve not just the Center's targets, but the ultimate targets; that is, how much better do heat transfer, hydrogen diffusivity, material packing, and material density need to be to reach the ultimate targets. Priorities should be assigned to which areas could be improved and which are beyond physical limits, etc.
- DOE and the Center should carefully discuss the scope of Phase III activities. Given that the system's architecture depends on the storage material and that a suitable material does not currently exist, building a complete prototype with controls may not be useful in the long run. Perhaps the resources will be better spent looking at alternate approaches.
- If the DOE Hydrogen and Fuel Cells Program (the Program) is going to keep funding research on hydrogen storage, it should consider a "reinvention" of the HSECoE into a new entity that keeps the core HSECoE capabilities intact and enables continued progress toward large-scale implementation by providing validating analyses of new developments from future hydrogen storage research. Some type of DOE-sponsored project should exist for the entire Program through Technology Readiness Level 7 on slide 45 of the SRNL presentation. A great deal of research and development continuity will be lost if DOE does not stay involved. Also, if DOE steps away from this project too soon, it probably will never get the credit it deserves for a successful commercial outcome. It would have been a bit easier to evaluate this project as a whole if the reviewers knew the outcome of the go/no-go decisions that are presently under consideration by DOE.
- A clear and detailed statement of the specific technical challenges and plans for addressing those challenges should be included in the plans for the Phase III effort. Specific attention should be paid to the evolving complexity of the AB-based system and whether those complications could be ameliorated in an alane-based hydrogen storage/delivery system.

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

Jamie Holladay; Pacific Northwest National Laboratory

Brief Summary of Project:

The objectives of this project are to address most of the engineering challenges for materials-based hydrogen storage for endothermic and exothermic chemical hydrogen and cryo-adsorbents and to provide feedback and recommendations on materials requirements. The project will demonstrate chemical hydrogen storage systems for light-duty vehicles and identify and develop solutions to overcome component materials deficiencies that affect performance in light-duty vehicles.



Question 1: Approach to performing the work

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

- The work is well organized and of extremely high quality. All milestones have been met, and several non-milestone achievements have been accomplished.
- Researchers investigated alane and ammonia borane (AB) materials systems and considered Type I and Type III cryo-adsorbent tanks and the use of friction stir welding as a joining technique. Their approach also included development of system models and experimental validation of these models, as well as component validation, prototype demonstration, and cost estimations. This approach is very good!
- The approach is generally effective and contributes to overcoming some barriers. Researchers demonstrated a clear pathway for meeting gravimetric and volumetric targets, but other targets are not being addressed (such as well-to-power plant efficiency).
- The approach is good. It is focused on the challenges of slurry flow management and settling behaviors. The design of the reactor, heat exchanger, exchange tank, and pump components are critical to chemical hydrogen storage system success. The project is focused on pressure vessel design and validation for adsorbent storage.
- The team worked with known materials to design systems for solid/slurry-based storage materials. This is a very challenging medium to work with and essentially a nonstarter for automotive use. Demanding automotive conditions, such as temperature, humidity, noise, vibration, harshness, etc., make moving anything other than gas or low-viscosity liquids very challenging. The complexities of and amount of hydrogen cleanup required by these systems start to approach those of onboard reformers, which the DOE Hydrogen and Fuel Cells Program (the Program) down-selected several years ago. Future work should shift emphasis to liquid materials that both simplify material movement and post-process H_2 cleanup. Volume exchange tank work should consider heat transfer issues that can cause hydrogen release on the fuel side.
- Modeling of reaction rates for alane shows good results. No clear justification was given for using polymer slurries as proxies for AB. It is unclear whether particle size distributions, particle shapes, and bulk densities were equivalent. Slurries appear to require periodic agitation. This is likely a non-starter for fuel applications.

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

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

- The accomplishments are impressive. The range of projects and technical challenges is unusually broad, and the combination of modeling and experimental work is particularly noteworthy.
- Milestones have been met or exceeded or the potential to do so has been shown.
- The volume exchange tank work was well done. This approach is also valuable for other fuel cell systems, including small and mid-sized portable units using other chemical hydrogen storage material approaches.
- A tremendous amount of work was accomplished in pushing these systems to their maximum. Of particular note is the work on membranes, which showed impressive results in durability. The team should, however, consider heat exchange between spent/unspent fuel that could cause premature hydrogen evolution on the fuel side. Perhaps a double-walled membrane could be considered. The extra volume and weight of such a solution should be accounted for in the overall system calculations.
- Researchers have made nice progress toward meeting the objectives and overcoming one or more barriers. They demonstrated a flow reactor with AB and AlH_3 at 45% loading, but higher loadings are needed if targets are to be met. The kinetics look decent for both AB and alane, but improvements are likely with other slurry media. Some important differences between AlH_3 and AB were identified: AlH_3 has no gas cleanup issues and flows well (hydrided and dehydrided), but it requires an extra mass of approximately 30 kg. Fully hydrogenated AB showed some issues with clogging, which should be addressed. The use of pleated membrane for a partitioned tank seems to work well, which may enable conformable tanks. The balance of plant and costing of an optimized design for the cryo-adsorbed tank look good. The team achieved costing for 135 cryo-adsorbed tank configurations. Most milestones were met or exceeded.
- Publication of a "tankinator" model for tank modeling allows for design optimization without extensive trial-and-error experimentation. Waterfall charts showing system improvements should be accompanied by credible strategies for achieving targeted improvements or some idea of how likely improvements are. The basis for the improvements should be explained and justified by preliminary experimental accomplishments.

Question 3: Collaboration and coordination with other institutions

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

- The Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center) is an excellent collaboration of industry, academia, laboratories, etc. This model should be emulated by other technical teams.
- This project features close, appropriate collaboration with other institutions within the Center; partners are full participants and are well coordinated.
- The breadth and diversity of this project demand close coordination with other institutions and partners. Management of these interactions and relationships is effective and results in the whole operation being significantly more than the sum of its constituent parts.
- There is good collaboration within the Center but limited work with outside investigators.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This is a key project that underpins the central activities of the HSECoE, and it is of general value to the wider hydrogen storage community.
- This project's relevance is limited because a significant part of the work is being carried out on materials that are not viable.
- The project partially supports the Program and DOE RD&D objectives. The impact of the cryo-adsorbed tank could be high. However, engineering efforts on the chemical hydrogen storage systems seem

premature. This project has revealed some interesting new issues (such as clogging with AB and the need for gas cleanup), but many of these issues could have been anticipated from materials studies. The real issues with chemical hydrogen storage materials remain with the regeneration efficiency, and it is unclear how much value further engineering studies can provide until this key issue is addressed.
- The bill of materials and cost estimation portions are relevant. Future work should shift emphasis on liquid materials that both simplify material movement and post-process H_2 cleanup. The volume exchange tank work should consider heat transfer issues that can cause hydrogen release on the fuel side. It is unlikely original equipment manufacturers will use complicated chemical hydrogen storage systems unless the systems can be dramatically simplified and the recycling energy issues of the materials can be resolved.
- Meeting the next DOE performance goals will be difficult for both chemical hydrogen storage materials and adsorption approaches.

Question 5: Proposed future work

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

- Future plans are sensible and build on progress made to date. Comments from last year's DOE Hydrogen and Fuel Cells Program Annual Merit Review have been carefully considered and addressed.
- Proposed future work includes cost and experimental validation of pressure vessel cooling and heat loss with tank design.
- It would be nice to see an increased focus on the sorbent tanks and cryo vessels—these have a larger chance of success for vehicular use. Understanding heat exchange issues for sorbent-based materials is key to designing high-capacity systems and the knowledge is mostly transferrable to new sorbent materials as they become available.
- Plans may lead to improvements, but they should be more focused on overcoming all barriers. Plans to design sub-scale prototypes for AB and alane are unlikely to make significant progress in overcoming barriers. Plans for a cryo-adsorbed prototype seem worthwhile and, although unlikely to meet all targets, the system design/engineering will be a valuable contribution. This type of tank may be an appropriate near-term solution over compressed gas.
- Given the recent work on well-to-wheels efficiency of chemical hydrogen storage materials, the Program should consider stopping work on these systems until a more efficient material is found. The Center should consider combining the cost model with other models developed in the Program.

Project strengths:

- This project's strengths include providing a system bill of materials, bladder concepts, and cryo-sorbent tanks.
- The work on the cryo-adsorbed tank is progressing nicely. This may prove to be a useful alternative to 700 bar compressed gas.
- This project features excellent organization and coordination, partnerships with strong groups and companies, and an interactive consortium.
- The approach of making engineering and design information available to the portable and stationary applications can be very valuable. The volume exchange tank and general slurry behavior are examples.

Project weaknesses:

- The project team did a good job, but perhaps they are going down a rabbit hole on slurry pumping for AB- and alane-type materials.
- The fact that the Center is working on proxy materials limits the usefulness of these results.
- The project objective is to demonstrate a hydrogen storage system that meets DOE 2017 targets for light-duty vehicles using chemical hydrogen storage, but efficiency remains a key barrier and is not being addressed.
- A lot relies on the need to have a well-behaved slurry that is higher than 50% wt.% AB, as well as a reliable and stable exothermic auger reactor. It is unclear whether the failure modes (or full failure mode and effects analysis) have been studied for the auger reactor and the ability to control the reaction region

location and length. Perhaps an intrinsic stability design can be included for the exothermic reaction scheme.
- There are no weaknesses evident from the material presented.

Recommendations for additions/deletions to project scope:

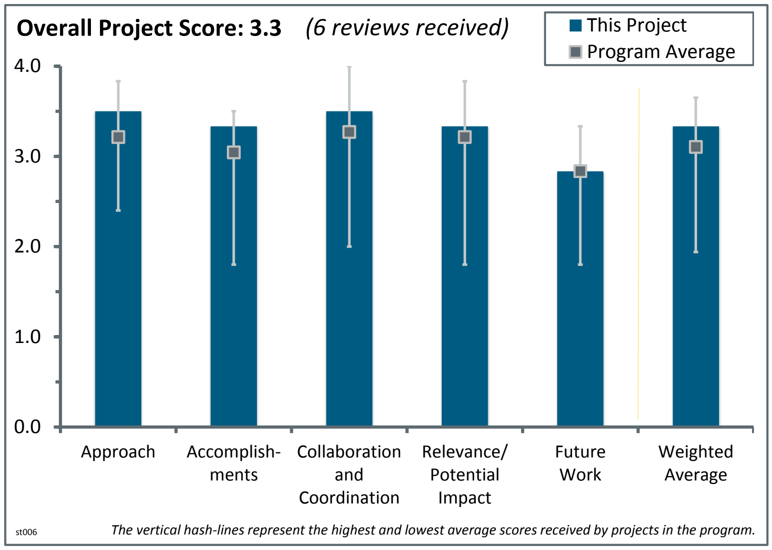
- The project team should reduce its work on slurries and increase its work on sorbent and cryo tanks.

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 leverages in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials-based hydrogen storage for automotive applications. The project has focused efforts over the past year on gas/liquid separation of liquid chemical hydrogen storage materials, hydrogen quality, integrated power plant storage system modeling, and risk assessment.



Question 1: Approach to performing the work

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

- The approach is well planned and executed. Coordination with partners is effective and productive.
- This project is part of the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center) and has been involved in a number of different critical tasks. The researchers' focus on identifying and sizing end-of-the-line purification systems is a good illustration of the positive attributes to which they contribute. United Technologies Research Center (UTRC) provides sound and solid work.
- UTRC's effort within the HSECoE embraces many barriers, but with particular emphasis on system weight and volume, durability/operability, and thermal energy management. The UTRC work is sharply focused on lingering system performance issues that must be addressed and mitigated, including gas-liquid separation, hydrogen purification (e.g., ammonia [NH_3] removal), particulate removal, risk abatement, and other issues.
- This is a well-formulated approach that addresses several important problems inherent in the successful implementation of a hydrogen storage/delivery system based on chemical hydrogen storage materials. The development of an efficient gas-liquid separator (GLS) for separating hydrogen gas from the spent liquid chemical hydrogen storage material and the development of an NH_3/particulate filter for purifying the hydrogen gas stream are especially critical to the ultimate deployment of a fully operational prototype system based on ammonia borane (AB). The design concepts and engineering implementation have been developed in a sensible and straightforward way.
- The approach is well formulated in that it is designed to develop and refine solutions for mitigating impurities (NH_3, borazine, and particulates), as well as understand the relative upstream flammability risk in using an AB slurry.
- No clear justification was given for using polymer slurries as proxies for AB. It is unclear if particle size distributions, particle shapes, and bulk densities were equivalent. Demisting is a common unit operation. It is not clear that a computational fluid dynamics model needed to be developed to accomplish effective gas liquid separation. Safety assessments need to include thermal runaway experiments. These are standard tests using methods, such as accelerating rate calorimetry, that are available at contract laboratories. These tests are generally mandatory for work with solids capable of exothermic reactions.

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

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

- The project achieved several targets.
- UTRC appears to have made excellent progress on every system performance issue it addressed in the past year. Results in the area of gas-liquid separation and NH_3 scrubbing are impressive and are essential to the success of the project as a whole. It appears that some impressive publications emanated from work done to date (as indicated in the extra slides).
- The filter developed here is a very valuable accomplishment. NH_3 filtering is valuable to AB systems and can also be valuable to other portable and small stationary fuel cell systems using other chemical hydrogen storage materials. The GLS design and model were well done, but it may be better to consider a cyclone separator. On the particulates slide (slide 19), the particle sizer looks like it had an upper measuring limit of 0.5 µ, which is 1/20th the <10 µ SAE International specification. If so, measurement ability should be extended up to 10 µ.
- Most milestones have been achieved. The carryover issue in the GLS remains to be solved. The NH_3 filtration work is impressive.
- Solid progress has been made on the development of a GLS test facility and GLS model development. In particular, careful attention was paid to characterizing the effects of a distribution in droplet sizes at the outlet of the GLS and to developing plans for integrating the GLS with the chemical hydrogen storage material thermolysis reactor. The onboard NH_3 sorbent filter simulation and experimental validation data are encouraging. However, removal of borazine contamination in the gas stream still remains an outstanding issue. Risk assessment comparisons on the flammability of solid AB versus liquid AB are providing useful information that will undoubtedly impact the ultimate selection of the most appropriate storage medium. Overall, the technical accomplishments in 2012–2013 are impressive in all areas of the project and should facilitate a smooth transition to successful development of a working subsystem in the Phase III effort.
- The researchers provided the NH_3 filter to Los Alamos National Laboratory for some testing with NH_3/borazine mixtures. It is unclear whether borazine decreases the efficiency of the NH_3 filter. One could imagine the borazine forming a weak complex with the $MnCl_2$ if NH_3 forms a strong complex. For the liquid separator, it seems like the vapor pressure of the carrier fluid is the key property defining the size of the GLS. If the Center were to use a liquid carrier with half the vapor pressure, it would be nice to know whether the size of the separator decreases by half. An analysis of liquid separator versus vapor pressure of a carrier solvent could be useful to target liquids with the appropriate viscosity and vapor pressure. There are questions about (1) whether there is any physical insight into how borazine might partition in the gas and the liquid droplets formed from the carrier fluid; (2) if borazine could form droplets on its own at a given temperature, e.g., below the boiling point of 55°C, and whether the droplets can be separated from the gas; (3) whether borazine could be preferentially soluble in the liquid droplets and thus be removed from the hydrogen gas; and (4) whether one could measure the enthalpy of dissolving borazine in different carrier fluids to see if this is a favorable physical reaction. If borazine is trapped in the liquid separator, it could be added to the spent fuel for regeneration. It is unclear what fluid is used for the alane carrier and what its vapor pressure and reactor size are.
- It will be interesting to learn how well the beta testing on the beta version of the graphical user interface model turns out. It will be a challenge but a critical output of the HSECoE to provide models that can be used by other researchers to help them test new ideas.

Question 3: Collaboration and coordination with other institutions

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

- This project's collaboration and coordination are very strong.
- The collaboration is well organized and effectively managed.

- The specifics of the UTRC collaborations within the HSECoE are clearly specified throughout the presentation slides. Coordinated efforts with Oak Ridge National Laboratory, Sandia National Laboratories, and BASF/Ford are highlighted.
- Collaborations with multiple HSECoE partners are listed for all of the tasks on the project. However, with a few exceptions, the specific contributions of the HSECoE partners are not specifically noted or acknowledged. Consequently, it is difficult to discern what contributions (if any) were made by the collaborating organizations.
- It was unclear from the presentation who did what. Nevertheless, the results from this project are critical to chemical hydrogen storage materials. The overall project looks like it was well coordinated and that all sub-elements received the right attention and effort.
- There was no mention of collaboration in the presentation.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- UTRC appears to do what is asked of it to help the HSECoE, and does it very well.
- At the present stage of the HSECoE project, everything UTRC is engaged in is pivotal to a successful outcome during Phase III. The project's relevancy is very high.
- The project provides important engineering support to several key areas of HSECoE activity.
- The GLS and NH_3 filter are critical elements of slurry AB hydrogen storage systems. (The GLS is also critical to AlH_3 slurry systems.)
- This project is an integral component of the overall HSECoE effort. In addition to supporting storage system modeling and integration activities in the Center, UTRC is developing important balance-of-plant technologies, including a gas-liquid separator for liquid chemical hydrogen media and sorbent filters for removing NH_3 and particulates from hydrogen gas liberated by thermolysis of AB. These activities directly support the HSECoE goals for storage system prototype development and are closely aligned with DOE's RD&D objectives.
- The relevance is limited because a significant part of the work is being carried out on materials that are not viable.

Question 5: Proposed future work

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

- Plans are aligned with long-term project objectives and with other HSECoE partners.
- A well-thought-out plan with associated workflow and schedule information is provided. However, it would have been helpful if specific, technical obstacles and plans for overcoming those obstacles had been included in the proposed future work plan.
- The plan forward considers all of the necessary elements, but it does not plan for the likely contingency for iteration on the Phase III components, system, model, or controls.
- Technologies developed for model materials may not be applicable to commercially viable materials.
- The UTRC future plans were covered on slide 20 of the presentation in a very general way. Much is left to surmise about the details of what will be done in the coming year. Even though it is obvious that UTRC is on an appropriate and effective path in its work, it would be reassuring to see a list of the specifics and an explicit statement of the expected outcomes.
- It would be useful for UTRC to provide some feedback to the HSECoE on an optimum vapor pressure for a carrier fluid. It is unclear how small the researchers could make the separator if the vapor pressure was reduced by 50%, or even 90%. There must be a size that is as small as it can get. Also, it is unclear if borazine can form droplets that can be trapped in a liquid separator. Besides vapor pressure and temperature, it is unclear what leads to droplet formation. Maybe UTRC could help reduce borazine with the liquid separator. The vapor pressure of borazine versus temperature has been published.

Project strengths:

- The research and development, planning and execution, close coordination with other HSECoE projects, and project leadership at UTRC are excellent. These factors greatly strengthen the project in terms of achieving objectives and mitigating barriers. The presentation was very well delivered—clear, crisp, and concise. The additional slides for reviewers were appreciated. It shows that UTRC is taking the reviewers' comments seriously.
- This project addresses several important technical problems that impact the successful development of an AB-based hydrogen storage/delivery system. The project team is well qualified, with expertise and background in all aspects of modeling/simulation and the system engineering needed to achieve the goals of the project. This work is an important component of the overall HSECoE effort.

Project weaknesses:

- It is unlikely that AB will meet the overall DOE hydrogen storage targets. Consequently, it is not entirely clear whether the work that has been conducted in this project will translate effectively to a system based on an alternate chemical hydrogen storage medium having improved material properties.
- The need for auxiliary equipment (demister, NH_3 adsorber, etc.) makes a marginal chemical hydrogen storage system even less desirable.
- It is not obvious that the project made extensive inquiries with manufacturers of gas-liquid separations equipment.
- The UTRC project shows no discernible weaknesses in approach/relevance, collaboration, or productivity.

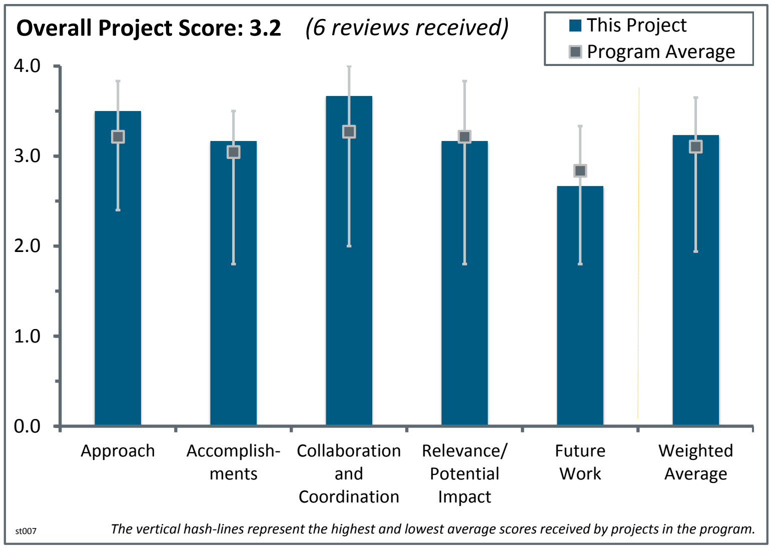
Recommendations for additions/deletions to project scope:

- More detail on future plans would be a helpful addition for reviewers.
- Insofar as AB is unlikely to be the storage medium that will be used in a practical storage/delivery system, the principal investigator and his team should consider how this work can be extended to address a storage system employing a different material (e.g., alane) with potentially superior storage/delivery properties.
- For the GLS, the project team should look into a miniature cyclone separator with tangential flow input. The axial flow GLS with swirl vanes is not a very efficient use of volume, and it is heavy. There should be cyclone versions available in the configuration and size needed, and if not, it is relatively simple to design, build, test, and iterate upon. It should significantly reduce volume and weight. The presence of swirl vanes in the axial flow GLS reagglomerates the input droplets on the blade surfaces then redistributes them downstream in a new droplet size distribution. The Weber and Reynolds numbers strongly affect this, and the shedding velocity profile and length scale in the vaned environment is difficult to model. In addition, using nitrogen to model hydrogen may strongly change the density-ratio-driven droplet breakup. The flow in a cyclone separator is much more controllable, predictable, and able to be modeled. For an absorbed system (MOF-5 assumed), there does not seem to be a plan to improve on the particle size diagnostic.

Project # ST-007: Chemical Hydrogen Rate Modeling, Validation, and System Demonstration

Troy Semelsberger; Los Alamos National Laboratory

Brief Summary of Project:



The objectives of this project are to: (1) provide a validated modeling framework; (2) provide an internally consistent operating envelope for materials comparison with regard to mass, volume, cost, and performance; (3) provide component scaling as a function of chemical hydrogen storage media and application; (4) provide the materials operating envelope required to meet the U.S. Department of Energy (DOE) 2017 targets; (5) identify and advance engineering solutions to address material-based non-idealities; and (6) identify, advance, and validate primary system-level components.

Question 1: Approach to performing the work

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

- The reactor designs and expanded scope of materials studies provide an excellent approach to the evaluation of the practical performance of this class of hydrogen storage materials.
- The project is charged with providing a modeling framework and systems validation for several key activities relating to chemical hydrogen storage material technology within the Hydrogen Storage Engineering Center of Excellence (HSECoE). This requires close control and integration of a broad and diverse set of subtasks and milestones. These are managed efficiently and effectively, creating an impressive operation for which the whole significantly exceeds the sum of the individual parts.
- The Los Alamos National Laboratory (LANL) approach embraces a well-conceived blend of technical tasks that address pivotal aspects of the hydrogen storage system, including component design/development/testing, system integration, performance modeling, and comprehensive system validation. The output of the LANL project factors into much of what goes on throughout the HSECoE as a whole. The LANL effort is properly focused and well directed; it addresses all of the critical barrier issues head on and it is difficult to identify any substantive ways to improve the overall approach.
- The general approach seems effective and there is a clear path to overcoming some barriers. It is nice to see alane slurry is being considered along with ammonia borane (AB). The project team may also want to consider $LiAlH_4$ because the regeneration is simpler. There is no clear path to improving well-to-power plant efficiency.
- The team is doing a reasonable job of addressing onboard issues, but optimization of an onboard system without considering the implications for the forecourt will likely lead to suboptimal solutions.
- The approach is adequate but it leaves room for improvement. The 50% alane slurry would never meet expectations. It is not clear why it was investigated.

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

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

- The reactor designs and expanded scope of materials studies provide an excellent approach to the evaluation of the practical performance of this class of hydrogen storage materials.
- The number of accomplishments laid out in the LANL presentation is close to overwhelming. Progress has been made on many fronts; gaps in performance versus targets have been reduced in several key areas; and the prospects for demonstration of a functional hydrogen storage system by the end of Phase III have been substantially improved. The accomplishments summarized on slide 31 of the LANL presentation for alane and AB represent important advances toward storage capacity targets. Especially impressive are the advances in reactor performance for both types of chemical hydrogen storage material.
- Accomplishments have been good, with evidence of significant progress toward the stated objectives. Particularly important outcomes include the optimization of chemical hydrogen storage material reactor conditions, the quantification of all gaseous products from AB fluid fuels, and the development of a regenerable borazine scrubber.
- The team has made significant progress toward the objectives and overcoming one or more barriers. It has made nice progress with demonstrating flow reactors for AB, alane, and methoxypropyl amine borane (MPAB), as well as characterizing reaction rates and impurity gases. These results are a nice confirmation of the viability of these flow systems. Identification of CAN-210-15 as a high-borazine absorber is an important step forward for the viability of any boron-based hydrogen storage system. MPAB (3.9%) results show promise because it remains a liquid after desorption—no slugging or fouling and only minor trace impurities. Slurry alane and AB results with an auger reactor also look promising, but higher loadings are needed to truly test slugging/fouling.
- The team achieved good results on system modeling. At the same time, the 50% alane slurry would never meet expectations and the materials with the higher alane content are hard to handle. It is unclear why alane was even evaluated.
- Although borazine and ammonia can be successfully scrubbed, logistics associated with their collection, recovery, and regeneration will make recovery difficult and expensive. It is hard to imagine going to higher (70%) loading slurries from 20%, where settling can be a problem already.

Question 3: Collaboration and coordination with other institutions

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

- There is clear collaboration with other institutions within the HSECoE; the partners are full participants and are well coordinated.
- It is clear that the LANL team is well connected with and integrated into the aggregate HSECoE. Interactions with DOE management and with other organizations that serve or assist the DOE Hydrogen Storage program were also highlighted. Much of what LANL does drives the research and modeling efforts in other parts of the HSECoE project.
- This project demands close collaboration and interaction with several other institutions, including the United Technologies Research Center, Pacific Northwest National Laboratory, and the National Renewable Energy Laboratory. The interactions are close and mutually supportive.
- This project features good team work; the team could benefit from participation of some additional chemistry partners, especially those manufacturing AB and related materials.
- There is excellence collaboration and coordination among team members and with the HSECoE, but there is no wider range collaboration.
- The project team needs to include fuel providers and well-to-wheels (WTW) modelers to look into forecourt implications.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The project is very relevant to the Hydrogen and Fuel Cells Program (Program) goals and objectives.
- This is a central, multidisciplinary project of high importance to the HSECoE's overall objectives.
- The LANL work scope contributes in a major way to the definition and refinement of the storage system operating envelope. This work includes identification and testing of engineering solutions to system component deficiencies, together with component function modeling and validation. As presented, the LANL effort is critical to the Phase III objectives and goals of the HSECoE. The tasks involving reactor functionality, fuel purification, and overall system optimization are producing pivotal results on the path to a target-meeting system. In short, the relevancy of the LANL project is at a very high level.
- The project partially supports the Program and DOE RD&D objectives. This project supports and advances progress toward meeting the Program's goals, but further optimization and new engineering concepts are not going to result in a system that meets all of the targets. The spider charts clearly indicate that the key challenge with AB and alane is well-to-power plant efficiency. The impact of this project is likely to remain low until new regeneration routes can be identified with improved efficiencies.
- This project addresses problems associated with the development of viable hydrogen storage systems based on chemical hydrogen storage materials. During the past year, the scope of the project has been greatly expanded to cover a much wider variety of chemical hydrogen storage materials, and thus it is now of much greater overall relevance to DOE objectives. However, like many of the chemical hydrogen storage material projects in the Hydrogen Storage program, its relevance is limited because the key problem of re-hydrogenation is largely ignored.
- Because these materials do not meet goals associated with fuel cost and WTW energy efficiency, specific work on hydrogen generation may or may not have relevance. Slurry pumping is likely a nonstarter for forecourt operations.

Question 5: Proposed future work

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

- The proposed future work builds on the achievements presented and is logical and sensible in terms of scope and objectives.
- Plans build on past progress and generally address overcoming barriers. The future work plan seems reasonable. Clearly higher loadings are needed for AB and alane. It may be worth considering other slurry media, such as those that undergo reversible (de)hydrogenation reactions. This will likely complicate the regeneration efforts, but it would be worth demonstrating.
- Future work is just a continuation of the current effort. Given that 2014 is the planned completion date, this section could have been more extensive.
- Continued work on marginal materials is of questionable value.
- This project is in its last year. Rather than gather further information on AB slurries that will not meet DOE targets, future plans should focus on obtaining at least some preliminary results on the liquid material.
- The proposed future work was presented in a somewhat sketchy manner. It appears to go forward in a logical way from the progress to date to the final stages of system testing (i.e., refinement of reactor experiments together with further research and development to mitigate the remaining barriers to a proof-of-concept demonstration). Like most of the other HSECoE presentations, the LANL presentation focused more on the accomplishments (of which there were many). The future plans for the remainder of the project deserved more emphasis and a bit more detailing.

Project strengths:

- This project features solid modeling work, good collaborations, and interesting results to date.
- This project is well coordinated with HSECoE. It has made steady progress with slurries and borazine scrubbers.

- The project team consists of an outstanding group of experts that has consistently obtained high-quality, well-analyzed results.
- This project clearly benefits from strong, intuitive leadership at LANL; excellent research planning and execution by people who are now at the cutting edge of hydrogen storage science and technology; and close coordination/collaboration within the HSECoE as a whole.
- Strengths of this project include dynamic interactions between capable partners, a good overview of strategic objectives, and objective down-selection and refocusing of resources.

Project weaknesses:

- The project remains too focused on AB.
- The choice of materials is an area of weakness. The collaborations still have room for improvement.
- The project is unlikely to make much of an impact on the well-to-power plant efficiency target, which is the key outstanding issue.
- More direct chemical input would be helpful (e.g., in choice of appropriate ionic liquids).
- This project has no weaknesses, but all should keep in mind that the projected Phase III spider charts are a picture of what might be if everything goes as well as is credibly possible. The researchers are hoping for an outcome that is still far from guaranteed.

Recommendations for additions/deletions to project scope:

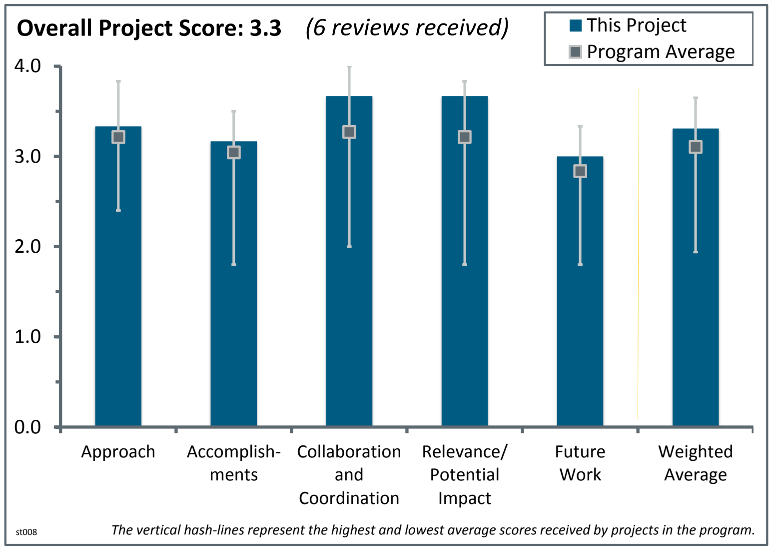
- The project is functioning just fine as is. The project team should keep up the great work.
- It is worth trying MPAB or other liquid hydrogen carriers as a slurry agent for alane or AB. Other slurry media should be considered for alane. Silicon oil is a reasonable first choice, but other liquids show much better kinetics. It may be worth investigating $LiAlH_4$ slurries because $LiAlH_4$ is much simpler to regenerate.
- The work on AB should be curtailed and the more generally relevant work on the representative liquid material should be expanded.
- Given the recent energy efficiency results and all of the difficulties associated with contaminants, flow assurance, etc., the Program should consider dropping the chemical hydrogen storage material work until more promising materials can be found.

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 objectives of this project are to: (1) develop and apply a model for evaluating hydrogen storage requirements, performance, and cost trade-offs at the vehicle system level; (2) provide high-level evaluation of the performance of materials-based systems; and (3) perform hydrogen storage system energy analysis to evaluate well-to-power-plant efficiency, energy requirements, hydrogen cost, and greenhouse gas emissions.



Question 1: Approach to performing the work

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

- This project features a good approach to addressing vehicle performance and energy analysis.
- The analysis approach is sound—using different drive cycles to run vehicle simulations provides a realistic assessment of fuel economy, range, onboard efficiency, and vehicle performance.
- As part of the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center), this project has a focus on developing cost/operating models for high-priority systems under consideration by the HSECoE. The National Renewable Energy Laboratory (NREL) led the Adsorption Center of Excellence (CoE) and is a logical location to provide the data needed to model a metal-organic-framework-5 (MOF-5)-based adsorption system. Because NREL has led the effort to validate the experimental techniques in other laboratories, data on MOF-5 should be reliable.
- The NREL effort is focused on seven technical barriers, all of which are pivotal to the success of the overall HSECoE project. The vehicle model is comprehensive and well validated. It is widely used within the HSECoE to evaluate candidate storage system designs on a common vehicle platform with consistent assumptions. In the presentation, NREL did a thorough job of documenting its approach—this was arguably the best “approach” documentation presented among the HSECoE projects reviewed at the Hydrogen and Fuel Cells Annual Merit Review and is a model others should follow in the future.
- The project is structured with two fairly separate approaches: modeling and simulation of hydrogen storage systems and an experimental component to determine materials properties for MOF-5-based adsorbents. The vehicle simulation work provides a common framework to evaluate various hydrogen storage technology options in a self-consistent manner. Some of the well-to-wheels (WTW) analysis appears to be a bit far afield for the work of the HSECoE because the Center does not consider off-board requirements.
- Having valid vehicle systems models is critical to designing appropriate storage models. The system selected is for a mild hybrid fuel cell vehicle. This is likely the appropriate powertrain configuration to select if limited to one choice. It would be nice to have at least a sensitivity analysis completed with a powertrain on the other end of the spectrum (e.g., range extender) to see what storage systems could be relaxed/modified, etc. Such a study would help original equipment manufacturers (OEMs) determine the best powertrain configurations for these storage systems.

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

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

- Based on the WTW analysis, these chemical storage systems have the highest costs and lowest efficiency numbers compared to compressed and cryo-compressed hydrogen storage systems. These are very important pieces of information and should have an impact on other projects that are dealing with chemical storage systems. The off-board regeneration should have a higher priority compared to work on chemical systems itself.
- Reasonable progress has been made since last year. Simulated vehicle performance results for AB slurry, alane slurry, and MOF-5 sorbent systems support the HSECoE's down-selection process for Phase III storage system designs and refinements. The project is developing a technique that removes helium calibration for standard isotherm measurements with a cryostat.
- Slides 13 and 14 of the NREL presentation tell most of the story. The results are very credible and very believable. No one should be surprised that compressed gas comes out on top. The increase in "system mass" from Phase I to Phase II may be a sign of the trend to expect by the end of Phase III. As the storage concepts are refined, the number, size, weight, and cost all tend to go up. The results leave the impression that progress toward goals from the end of Phase I to the end of Phase II has been incremental at best. Some breakthroughs are needed across the HSECoE in Phase III.
- The model does a good job of providing guidance to the system developers; however, it seems that the majority of the work was gathered from other contributors—the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model; Autonomie; OEMs; etc. It seems like most of the work was coordinating with existing models. This is not a criticism—the principal investigator (PI) leveraged existing models and eliminated redundancies. It is just hard to give the project a 4 for work that was not necessarily all original.
- The modeling and simulation results are good, but the material property input to the Center appears to be lagging—it is unclear how much more materials information is needed, but the experimental apparatus gives unreliable results at temperatures below about 40 K. The vehicle simulation results show that there is not a large difference in the gravimetric and volumetric densities or fuel economy for all 13 system variations that were analyzed. None met the DOE targets based on the current technology embodied in the HSECoE system designs. Breakthroughs in materials properties or some innovative systems concepts appear to be needed to enable the DOE targets to be achieved. The project team should also provide a better description of the materials properties work and how the information can be used by the Center.
- In these multilayered "analysis projects," it is a difficult to tell who is doing what analysis, but it is obvious that they are all working together, which may be more important than assigning specific credit. It is beneficial to see that the modeling work shows that the fuel cell vehicle drive performance with the various storage systems appears to satisfy the various drive cycle demands. One part of the HSECoE analysis that really stuck out was the system volumetric size in liters required to carry 5.6 kg of usable hydrogen. It was not directly listed but one could derive the system volume, in liters, for the various storage systems under investigation on slide 14 from the gravimetric density (grams H_2/kg system) and volumetric density (g H_2/liter system). For example, the system volume of 700 bar compressed gas can be derived from the volumetric density, which is 25 g H_2/liter of system at 700 bar. For a 5.6 kg system, the system volume is about [5,600 g H_2]/[25 g H_2/liter], which results in a 224 liter system. For the HexCell at 17.5 g H_2/liter and the modular adsorption tank insert (MATI) at 20.7 g H_2/liter, this comes to 320 and 270 liters, respectively. From a volumetric standard, this seems to be an eye opener. It would be fair to point this out and then focus on the positives of the sorbents, such as, perhaps, greater safety and lower pressure. (It is unclear what the operating temperature and pressure are for the sorbents.) The PI suggested that "they were close" on the volumetric targets. It seems the sorbents are not so close to the 40 g H_2/liter DOE target for 2017. It is unclear if a 300-liter system would fit into a "mid-size class family sedan." If the above approach to estimating the system volume is incorrect, then it would be valuable to include the system volume in the table of results to prevent others from making the same mistakes. It was a little difficult to follow the materials testing results because they were specifically used to validate the models. It was unclear if it was gravimetric density at sub-liquid nitrogen temperatures. The researchers are trying to do some tricky measurements at temperatures below 77 K. It is interesting that this has not been done previously

elsewhere, and if not, the researchers should take more credit for pioneering work. It is unclear what the target storage temperatures are for the MATI and HexCell sorbents, whether the model suggests going to temperatures below 77 K will improve capacity that is worth the extra cost, and if there is an added cost to systems operating at temperatures below liquid nitrogen temperatures. This could be made more clear in future presentations. In the comments to the reviewers' slides, the PI suggests that materials development will be further reduced to provide more resources to modeling. It is unclear if the researchers got close enough to solving the problems with the sub-liquid nitrogen temperature measurements to bring the effort to completion, for example, regarding the unknown pressure dependence and how/why it is affecting the measurements.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration and coordination are very strong.
- It seems that all relevant partners are involved.
- NREL has strong collaboration with other HSECoE partners. Such collaboration helps this project to produce results seamlessly and cost effectively.
- The collaboration is good across the HSECoE as well as with other teams involved with production and delivery of hydrogen by various pathways.
- The NREL project is clearly tightly coordinated with the other partners in the HSECoE. To be as effective as it is, the collaborative relationships must be very well established. This seems to be the case across the entire HSECoE.
- The collaboration is excellent because of the HSECoE. This is a model that all should follow. The project team demonstrated good coordination to leverage work from other teams such as the GREET model, H2A model, etc. The coordination with OEMs is critical for this type of task—the PI is working well with Ford Motor Company in particular to develop models.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Vehicle performance predictions and WTW studies are very important for future economic decisions.
- These models are critical to providing boundary conditions for good storage system designs—they provide insight into the operating conditions required for automotive applications.
- The modeling effort gives a side-by-side comparison of the systems under investigation. It points to specific strengths and weaknesses of the different systems and confirms that nothing is perfect.
- NREL focuses on the impact of storage system design on vehicle performance. These analyses allow the Center to assess the performance of various designs for the hydrogen storage system to guide the engineering effort in the most beneficial directions.
- This project applies the vehicle performance model Hydrogen Storage Simulator to evaluate the key performance metrics for various hydrogen storage options in support of the HSECoE's design selections. The second (and smaller) part of this project focuses on measuring MOF-5 isotherms at <75 K.
- NREL's contribution to the HSECoE in the modeling/system analysis area in a sense drives everything that goes on in the rest of the project because it provides a snapshot of where things stand with respect to vehicle performance, energy efficiency, and cost at all stages of the research and development (R&D). This is particularly important as the project heads down the stretch toward completion because it helps to identify where the remaining R&D should be focused.

Question 5: Proposed future work

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

- The proposed future work is appropriate—the project is 70% complete. If possible, the PI should add sensitivity analysis for sorbent tanks for a range extender fuel cell powertrain.
- The proposed future work is basically a continuation of the current work (minus the energy analysis portion). It does not appear that any new high-impact results should be expected this year.
- It will be helpful to include the volumetric system size as well as the gravimetric system size in future presentations.
- The vehicle performance modeling and analysis must continue to the end of the HSECoE project. It will provide the bottom line to the collective work of all HSECoE participants. The media engineering aspect, while important in some respects, may not be as critical down the stretch as the modeling/analysis.
- It seems that two additional years is a very long time to complete the remaining 30% of project content.
- The future work plans will continue to focus on evaluating the impact of system changes in Phase III storage system designs. It is good that the energy analysis work is complete because the Center was not intended to study off-board issues. The analysis to date assumes a fixed amount of hydrogen contained in the storage system. It would be instructive to redo the analyses on a fixed-volume basis. Fuel cell electric vehicles (FCEVs) will have a fixed packaging volume for fitting the storage system on board the vehicle. Greater discrimination between the various storage concepts could result from a fixed-volume analysis.

Project strengths:

- This project features good coordination with other modeling efforts being pursued by DOE, OEMs, etc.
- NREL has extensive experience in vehicle performance analysis.
- The coordination with HSECoE team members is an area of strength.
- Based on $100,000 per year of funding, NREL's productivity and level of accomplishment are huge. The NREL work is well focused and expertly directed. The presentation was easy to follow and appreciated.
- The vehicle simulation model is a major accomplishment of the NREL effort. It allows for comparison of various storage system concepts on a consistent basis.

Project weaknesses:

- This project has no obvious weaknesses. A great deal of meaningful work is being done at a very low cost to the overall HSECoE project.
- There is a lack of variation in powertrain configurations.
- The progress in MOF-5 isotherm measurement appears to be slow, perhaps due to limited funding.
- Getting across how the NREL experimental effort—low-temperature adsorption—helps to improve or validate the modeling is an area of weakness. The project team should provide a clearer picture of the advantages of the sorbents (and chemical storage) systems compared to 700 bar compressed gas.
- The summary page at the end of the presentation is exactly the same as the summary page used during the 2012 presentation. The summary slide should also summarize accomplishments.
- The information needed by the HSECoE on the adsorption properties of MOF-5 is not well described. There also appear to be experimental difficulties in obtaining this information at low temperature.

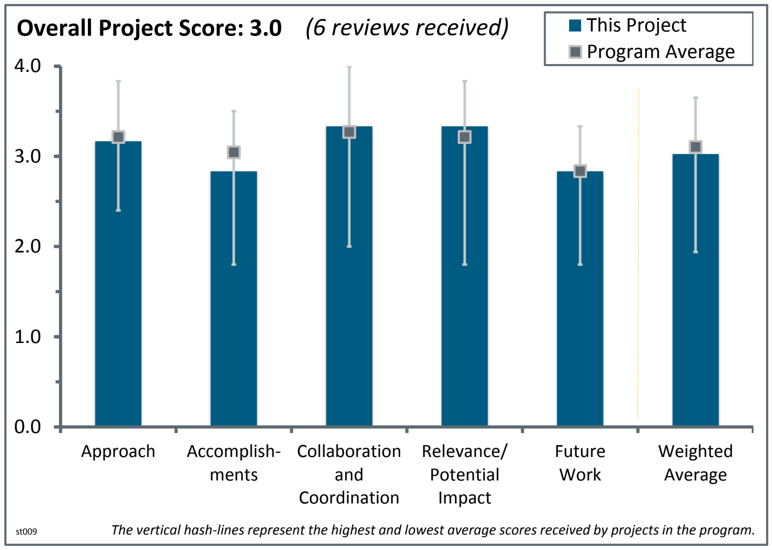
Recommendations for additions/deletions to project scope:

- The project team should keep up the good work.
- The project team should add range extender powertrain sensitivity analysis.
- The simulation work (vehicle performance and WTW) has no correlation to the material characterization. It is unclear if this project is the best platform to address this topic.
- It would be instructive to redo the analyses on a fixed volume basis. FCEVs will have a fixed packaging volume for fitting the storage system on board the vehicle. Greater discrimination between the various storage concepts could result from a fixed-volume analysis.

Project # ST-009: Thermal Management of Onboard Cryogenic Hydrogen Storage Systems

Mei Cai; General Motors

Brief Summary of Project:



Objectives of this project are to: (1) develop detailed simulation models for adsorbent systems; (2) develop detailed transport models to include adsorption and heat transfer to guide system models; (3) install and test a cryo-absorbent apparatus containing metal-organic-framework-5 (MOF-5) powder; (4) experimentally validate flow-through cooling of an MOF-5 powder bed during charging; (5) utilize a desorption model to optimize a resistance heater design; and (6) experimentally validate a desorption model with a helical coil resistive heater in a cryo-adsorbent apparatus. The project will also determine the engineering properties of materials and assists in the development of an integrated modeling framework.

Question 1: Approach to performing the work

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

- The overall approach is excellent, with very logical steps in experimental validation and feedback with the modeling. The critical barriers of refuel time, mass, and volume are being addressed well.
- A well-formulated approach incorporating modeling and simulation of thermal transport, thermal characterization in a fully instrumented cryo-adsorption test system, and development of an optimized resistive heater design has been employed in this project. The approach focuses on specific milestones established by the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- This project is a continuing part of the HSECoE activities with General Motors' (GM's) specific focus during the current review period on the analyses and testing of adsorbent storage system using MOF-5 media. The objective and scope are fully supportive to establish the potential and determine limitations of this sorbent to meet several performance targets associated with adsorption and desorption rates, including using internal heaters and the thermal enhancement additive expanded natural graphite (ENG).
- The approach of simulation model development and experimental validation is appropriate and has been performed well. However, one iteration with one material is not sufficient for either validating or improving the models. It is unfortunate that there was not more focus on this earlier in the project because it should have been possible to achieve much more in the given time frame. A plan for transferring and continuing this effort appears to be in place, so it is important that the transfer and further efforts are monitored and given a high priority.
- The GM work is directed at four key barriers: capacity, energy efficiency, charging/discharging, and thermal management. The overall effort includes modeling together with experimental model validation and the investigation of essential engineering properties of MOF-5. The major emphasis appears to be on aspects of the fueling system related to recharging of the MOF-5 bed and GM seems to be the HSECoE partner most heavily focused on this critical aspect of the hydrogen storage system. The GM approach to its role in the HSECoE is generally effective; however, it is not clear that the approach for Phase III will close the remaining gaps. It seems like there is more to be accomplished than GM's resources for Phase III will support.
- The approach is adequate.

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

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

- GM has made significant technical accomplishment in line with its milestones and contributions to the HSECoE project. The development of an experimental test station and completing a first round of validation of modeling efforts with experimental data is extremely important and should continue to be refined. It would have been preferable to have arrived at this point earlier in the project.
- Good progress was made on understanding the thermal characteristics during adsorption and desorption from MOF-5 in different sample configurations. A useful analysis was performed on the refueling times that would be achieved from “stick-like” and “hockey puck” sample configurations with varying dimensional aspect ratios. This led to at least a notion of what kind of sample configuration might be needed in a prototype system. Researchers evaluated the performance of a helical coil resistance heater for efficient desorption of hydrogen from cryo-adsorbed MOF-5. This should be helpful in the development of an efficient prototype system by the HSECoE in Phase III.
- Progress is modest; only some expectations have been met. The presenter showed deficiencies in his understanding of the heat transfer events. Unlikely to use the modeling results in real-life applications.
- Conventional thermal modeling was done using two different-sized test vessels (e.g., 3 liters [L] and 200 L), while cryogenic experiments were performed on a 3-L bed containing MOF-5 powder. Thermal measurements were also performed on compacts of MOF-5. While these analyses and measurements are useful for developing prototype adsorbent hydrogen storage systems, the researchers have not been able to design a configuration capable of meeting desorption target performance levels within mass and volume constraints. The researchers also performed useful thermal conductivity tests on ENG-MOF compacts that yielded some improvements in behavior.
- GM reported significant progress toward meeting some performance targets, but there are still a few gaps. Modeling studies show generally consistent agreement with measurements, but it seems that the models may need to incorporate some yet unidentified factors to produce tighter fits to experimental data. The pellet size/shape optimization result is interesting and potentially very significant. The modeling results for the 200 L tank are in serious need of validation.
- The completion and use of the experimental setup is critical to this project. The results in desorption performance using model and experiment are very promising. It does not appear that the 4 L over the limit heat exchanger would seriously jeopardize the overall full-scale storage goals, and it may be improved upon with other geometries—perhaps an axial or radial heat exchanger asymmetry to optimize the time-dependent three-dimensional temperature profiles.

Question 3: Collaboration and coordination with other institutions

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

- Collaborations exist and are well coordinated.
- There is very good coordination and interaction among all of the partners. This is impressive.
- Good coordination was shown with Ford Motor Company and BASF partners on characterizing properties and behavior of the MOF-5 adsorbents. The cryogenic testing complemented the design and modeling efforts of other HSECoE partners.
- Collaborations with multiple industrial, academic, and national laboratory partners are evident. These collaborations have served to enhance and leverage the GM effort in this project. There is a significant effort at Savannah River National Laboratory on thermal management as well. It would have been helpful if the division of effort between that project and this one had been more clearly delineated.
- The collaboration relationships outlined in slide 19 of the GM presentation provide a clear picture of how GM connects and coordinates with other members of the HSECoE.
- Technology transfer by making the models and experimental equipment available to the HSECoE is critical for future work. It was not abundantly clear from the presentation how much interaction on modeling efforts and data sharing occurred within the HSECoE or externally.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This project is aligned with the DOE Hydrogen and Fuel Cell Program's RD&D goals.
- The systems modeling and experimental work on cyrosorption materials is highly relevant and critical to DOE objectives.
- This project is critical in enabling one of the few realistic options for hydrogen storage in light-duty FCEVs.
- This project has reached the stage where it is making some significant contributions to meeting DOE storage system performance targets in the area of recharging and thermal management. System capacity and energy efficiency seem to be getting less emphasis, perhaps because they are covered at a higher level of effort by other HSECoE partners.
- Understanding heat transport issues and implementing effective thermal management approaches are vital for developing an adsorbent-based storage and delivery system that can operate with charging and discharging rates compatible with effective fuel cell operation. The project is an integral component of the overall HSECoE effort, and it directly supports the DOE RD&D objectives.
- Assessments of MOF powders and compacts with the ENG additives were valuable to the adsorption storage system development effort within HSECoE. This information provided some validation of design features to improve performance levels. However, thermal management issues still limit these storage devices from meeting critical mass and volume targets.

Question 5: Proposed future work

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

- It is excellent that the test apparatus will be used for HSECoE Phase III efforts. Hopefully, it will be used with the other cryo-absorbent architectures and at full scale. The plans are spot on.
- This project is nearly complete (85% as of March 2013). Plans are in place to complete the technical activity and fully document the results. It will be important for the PI and her team to ensure that the experimental and simulation results are communicated effectively to the rest of the HSECoE team. (GM will continue as a consultant to the HSECoE in Phase III.)
- The future work is not clearly defined; it is just a continuation of the existing research.
- GM will have a significantly reduced role during Phase III of the HSECoE program, and the former principal investigator (PI) from GM retired about a year ago. Hence, it is not clear whether GM will contribute much value in the future activities beyond a vague consultation role.
- The meaning of "prepare cryo-adsorbent test apparatus plus associated instrumentation for continued usage by the DOE HSECoE as needed in phase III" is unclear. It is unfortunate that GM will not continue with direct experimental and modeling work. It is critical that there is strong future advisory participation by GM in the HSECoE—not just at a bird's-eye and management level, but also very much at a research and development level.
- The proposed future work (slide 17 of the GM presentation) is not very exciting to say the least. "Document, polish, and consult" seem to be the operative words. One gets the sense that GM will not be doing much more experimental validation, and perhaps parts of its effort will be phased out.

Project strengths:

- This project features good modeling work and a good project team.
- GM researchers have performed unique cryogenic testing of adsorbents in support of modeling efforts. The findings are valuable to the hydrogen storage community.
- The coordination among partners and the interrelation between experiments and models are strengths of this project.
- The measurement science and engineering appears to be very good work that is being expertly planned and executed.

- A well-qualified team is conducting the technical effort. The GM-led team provides a good connection between the HSECoE and a major automobile manufacturer. The project incorporates solid elements of simulation/modeling and experimental work to address a problem that is vital in the development of a practical hydrogen storage prototype system based on cryo-adsorption.
- An experimental apparatus was developed and used to test and validate the model simulations. This is very important and should be the focus of further work. It is important because MOF-5 is unlikely to be the ultimate storage material; therefore, the modeling will become increasingly important in the optimization of both materials and systems until the ultimate materials are developed, as well as a guide to the determination of the materials properties that need the most improvement.

Project weaknesses:

- The project has no obvious weaknesses. The overarching problem is that MOF-5 will likely not be able to meet the DOE targets for hydrogen storage. An obvious question is whether the work conducted on this project will be fully transferable to another, more suitable, material if/when it is identified.
- Chances are low that MOF-5 will end up in real-life applications.
- Some key technical staff members are no longer working on this project, impacting both the GM modeling and testing contributions to HSECoE milestones. Questions remain whether GM will retain the cryogenic test facility and whether experienced laboratory staff will be available to support future testing.
- It is unclear how much coordination and collaboration have taken place on this project within the HSECoE and with international experts regarding incorporating existing experimental data into the task of validating the simulation models that have been developed. It is somewhat concerning that the MOF-5-centric approach may not challenge the modeling efforts extensively enough to make the simulation models sufficiently accurate for a wide range of physisorption materials.
- The modeling results appear to be approximations in some cases. The functional forms of the model curves do not always match the experimental curves. It is not clear how serious an issue this is. Thermal energy flow, in particular, is often hard to model. Perhaps the GM modeling results are the best one can hope to achieve at this time.

Recommendations for additions/deletions to project scope:

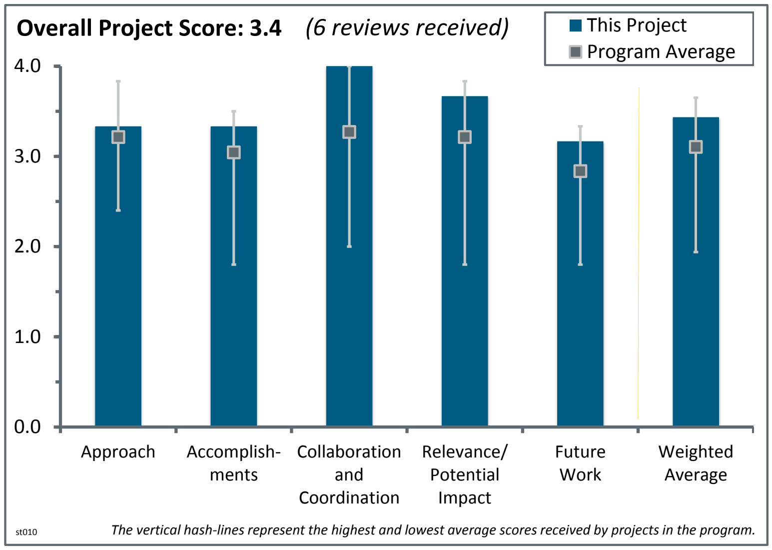
- The remaining technical obstacles and challenges should be discussed in a straightforward but detailed way. There are questions about what the major risks are and what risk mitigation strategies are in place.
- Papers should be prepared and submitted for publication reporting on cryogenic testing of the prototype beds and MOF-5 adsorbent properties. Prior modeling and test results should be fully shared with other HSECoE partners.
- Time is running out, but it would be nice to test the current models against data of a promising adsorption material or two that is dissimilar to MOF-5 in as many physical properties as possible. This would help determine the robustness of the models and aid in their further improvement.
- The future plans slide invoked concern about the extent to which GM can effectively close gaps and demonstrate the achievement of “Specific, Measurable, Achievable, Relevant, and Timely” (SMART) milestones in the coming year.

Project # ST-010: Ford/BASF-SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

Mike Veenstra; Ford Motor Company

Brief Summary of Project:

The objectives of this project fall under three tasks. Task 1 is to develop a dynamic vehicle parameter model that interfaces with diverse storage system concepts. Task 2 involves the development of robust cost projections for storage system concepts. Task 3 is to devise and develop system-focused strategies for processing and packing framework-based sorbent hydrogen storage media.



Question 1: Approach to performing the work

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

- The approach was very well balanced.
- The project is well organized, with clear roles and responsibilities for each team member.
- The approach has many well-considered features, including coordination of trade-off decisions, identification of strategic decision points, development of milestone criteria, spearheading of the go/no-go process, model development, failure modes analysis, and system ranking. The materials development and property measurement tasks are well thought out and sharply focused on critical technical barriers.
- The project team has adopted a well-reasoned approach for selecting suitable adsorption media, establishing design/performance trade-offs, and understanding and improving thermal conductivity in metal organic framework-5 (MOF-5) in different sample configurations. This information is important for developing and implementing an optimized prototype system.
- The approach was adequate.
- D. Siegel of the University of Michigan (UM) has the role of the system architect for the sorbent option. M. Veenstra of Ford Motor Company provides the original equipment manufacturer (OEM) perspective in developing fuel cell models, supporting cost studies, providing failure mode and effects analysis (FMEA) guidance, and ranking systems.

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

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

- A large amount of very useful data has been collected; this is critical to the success of the overall Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center) project.
- Numerous milestones were achieved or exceeded; several key system targets were met. Four high-importance system performance parameters were identified and addressed: fuel economy, driving range, vehicle acceleration, and cost. Ford performed a rational down-selection to MOF-5. Ford identified pathways for reducing the number and nature of potential failure modes. Ford achieved impressive results relevant to thermal conductivity issues; for example, the expanded natural graphite (ENG) additive improves thermal conductivity. In summary, it seems like every research and development (R&D) activity bore substantive fruit.

- Ford has done good work in performing FMEA for the sorbent option. The principal investigator (PI) presented new results on evaluating homogeneity of MOF-5 powder, pellets, and pellets with 5% ENG in terms of variations of density, particle size distribution, permeability, and thermal conductivity. The PI also discussed new data on the effects of humidity and air exposure and dust ignition safety. The data may not have value in the long term because it is specific to MOF-5, a material that does not meet storage targets, but the procedures and methods for FMEA should be useful for other promising sorbents. The PI presented old data on the impact of MOF-5 densification on hydrogen uptake, gravimetric and volumetric capacity, thermal conductivity, and permeability. The new data on kinetics and cycle testing should be useful.
- The accomplishments are very good. The only issue is that MOF-5 probably will not be the final material in a car. But it is required that programs such as the DOE Hydrogen and Fuel Cells Program also fund high-risk research, which this research should be considered.
- Although the quality of research is high, the results obtained are rather modest. It does not look like MOF-5 is going to end up in real applications. The presented results raise the question of whether MOFs are an appropriate hydrogen storage media for automotive applications at all.

Question 3: Collaboration and coordination with other institutions

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

- This project features an impressive list of collaborations.
- This project is highly collaborative.
- Ford appears to be well connected with all Center partners where responsibilities overlap. It appears from the collection of HSECoE presentations that the overall coordination of effort is at a very high level and that all appropriate and necessary collaborations are going along smoothly. Ford comes across as a major player with significant responsibility in the HSECoE.
- Excellent collaborations with other Center partners are apparent and are reinforcing the solid technical progress that is being made in this project. The perspective and system context provided by the participation of a major automobile manufacturer in the activities of the Center are extremely valuable.
- The collaborations with UM and BASF seem to be very effective, although UM's contributions in fiscal year 2013 were not clearly identified.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The project is relevant to the Hydrogen and Fuel Cells Program and DOE RD&D goals.
- The project objectives are clear, well defined, specifically oriented to address DOE systems level targets, and critical components of the HSECoE project.
- Ford is a major contributor to the HSECoE effort; its activities within the Center are focused on all hydrogen storage system barriers. It functions at both the executive and working levels of the project. Ford brings an automobile manufacturer's perspective to the project, provides leadership in a number of critical areas, and contributes effectively to key R&D and modeling tasks. The work done by Ford embraces all critical barriers to a successful outcome for the HSECoE. Much of the outcome of the Ford effort contributes to activities performed by other Center partners, or so it seems.
- This project is providing vehicle parameter modeling, system cost projections, and sorbent-media processing strategies that directly support the HSECoE mission. In addition, the participation of a major automobile manufacturer (Ford) in the planning and execution of the Center activities provides an important "real-world" perspective and validation of the overall HSECoE effort. The project directly supports the DOE RD&D goals for development and testing of a viable hydrogen storage system.
- The objective of this project is to design innovative material-based hydrogen system architectures to meet the DOE performance and cost targets. Even at the start, it was recognized that a storage system could not be engineered to overcome the limitations of the materials that are currently available. The hope is that the analysis and characterization methods and components developed in this project will be useful and relevant when new, promising materials are discovered by others.

- The risk analysis work is very important. In addition, Ford's work on media compaction, air exposure safety assessment of MOF-5, and neutron imaging of MOF-5 (in collaboration with NIST) are all highly relevant areas of research for sorbent-based hydrogen storage systems.

Question 5: Proposed future work

This project was rated **3.7** for its proposed future work.

- The proposed future work is very good and necessary.
- The future work is in line with the project's proposed work. It is important that all of the data and knowledge generated from this project be made available to the HSECoE and the DOE Hydrogen and Fuel Cells Program for future work and that the expertise is not lost as the project comes to an end.
- The future work is clearly laid out. BASF's work on scale-up to prepare kilogram quantities of MOF-5 is essential if the sorbent work continues in Phase III. The proposed work on thermal conductivity enhancement needs to be justified with a defensible conductivity target. The scope of work on failure modes could be curtailed because a noteworthy failure mechanism has not been identified. The proposed work on model development and validation is difficult to judge because of the involvement of other partners, including Savannah River National Laboratory, United Technologies Research Center, and the National Renewable Energy Laboratory.
- Phase III tasks are focused on engineering concept demonstrations, material property enhancements (e.g., thermal conductivity of a MOF-5 bed), enhancing system operational robustness, and system engineering validation. The goals for Phase III are presented in sufficient detail to give the reader a clear picture of what will be done and why. The future work proposed by Ford is well aligned with what was learned in Phase II and focuses on meeting the crucial "Specific, Measurable, Achievable, Relevant, and Timely" (SMART) milestones.
- The near-term plans follow directly from the Phase II effort and focus on important Phase III SMART milestones. The plans are clearly stated and address important system development issues. However, plans to achieve the specific milestone of "enhancing thermal conductivity beyond 10% ENG at operating temperatures" (slide 25) should be developed in greater detail (i.e., it is unclear what will actually be done to improve the thermal conductivity beyond the level achieved in 10% ENG samples).
- The proposed future work is somewhat poorly defined. This may be the result of rather modest success to date.

Project strengths:

- This is a good proof-of-concept type of work.
- This project has strong collaboration with BASF, the material supplier. The facilities and experience at Ford and BASF are definite assets.
- The presentation included excellent slide formatting to illustrate main points and it was well presented by the PI. The viewer is left with the impression that the project team did a significant amount of good work and made major steps toward achieving system targets.
- A well-qualified team is making excellent progress on all experimental and modeling efforts. The involvement of a major auto manufacturer in the technical activities and management of the Center is extremely valuable.
- This project has accomplished a considerable amount and achieved a wide range of experimental measurements of engineering properties of MOF-5-based hydrogen storage materials. This information is critical for the validation and improvement of HSECoE modeling systems. In addition, extensive FMEA was done to identify the weak links in the application of these materials to real-world application. This provides valuable insight and an OEM perspective within the areas of material and system improvements that will be needed for successful commercialization of fuel cell vehicles using adsorbents for hydrogen storage.

Project weaknesses:

- There were no detectable weaknesses one could attribute to this project.

- There are no real weaknesses in the project team or work. The team should continue to develop characterization methods using MOF-5 as the surrogate material.
- The material used to evaluate the concept has little chance to be used in real-life applications.
- An explicit and detailed statement concerning the technical obstacles, challenges, and risks that must be addressed in the Phase III effort is needed. Without that information, it is difficult to discern how development and engineering priorities were established.
- With the down-select, the focus of this work is now exclusively on MOF-5. At the same time, it is recognized that MOF-5 will not meet DOE targets. A viable physisorption storage material may ultimately not even be a MOF or related material. This means that the materials improvement methods, measurement techniques, and systems analysis tools being developed in this project must work for a wide range of materials to be discovered in the future. While studies have been performed within the HSECoE on activated carbons as well as MOF5, a concern is that it is not clear how representative the current MOF-5 analysis may be for a full range of adsorption materials. Without applying much of the same analysis to a significantly different physisorption material, it is hard to know: (1) how representative MOF-5 is for most adsorption materials in real-world systems, (2) how useful these analyses and models will be for other materials, and (3) what likely range of variations in all of the materials properties and performance being evaluated can be expected.

Recommendations for additions/deletions to project scope:

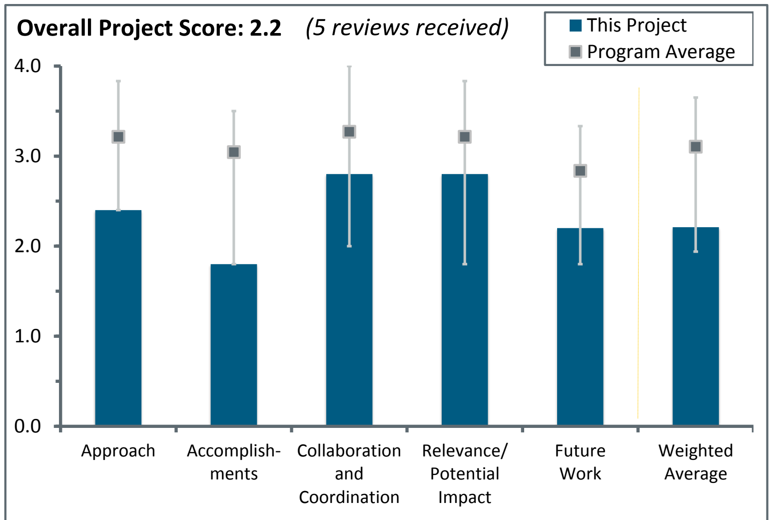
- Ford has a key role in the project and needs to remain a primary participant. This project has reached the point where the scope is honed to achieve a successful outcome. There is no need to change anything in Ford's future plan.
- There is no need to add or subtract tasks. DOE needs to make sure that the data and methods are properly documented and available to organizations outside of the HSECoE.
- The project team should look at density homogeneity within the single pellets with in-situ neutron tomography/radiography.
- It is highly unlikely that a system based on MOF-5 will meet the DOE targets for both gravimetric and volumetric capacity. It would be helpful if at least a pathway to identifying an optimum adsorbent system could be provided.
- A succinct set of similar experimental and modeling analysis should be performed on a promising physisorption material that is as different from MOF-5 in as many of its physical properties as possible. This would help to evaluate (1) how representative MOF-5 is for most adsorption materials in real-world systems, (2) how useful these analyses and models are for other materials, and (3) what likely range of variations in all of the materials properties and performance can be expected.

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

Peter Pfeifer; University of Missouri

Brief Summary of Project:

The objectives of this project are to fabricate boron-doped nanoporous carbon for high-capacity reversible hydrogen storage and to characterize materials and demonstrate storage performance. The project aims to create high-surface-area material and subsequent monoliths with minimum pore space for high volumetric storage capacity. Materials will be doped with boron to increase binding energy for hydrogen. Material properties will be characterized, and hydrogen sorption kinetics and temperature evolution during charging/discharging of the material/monoliths will be determined.



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

Question 1: Approach to performing the work

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

- The work examines several nanoporous carbon materials for their hydrogen sorption properties. The approach to the work is logical and step-wise. The investigators examine the processes to create high-surface-area monoliths of nanoporous carbon, then examine the doping of these monoliths with boron as well as characterize the hydrogen storage performance of these materials. The investigators present a predicted storage capacity as a function of boron doping wt.%. This predicted performance exceeds the U.S. Department of Energy (DOE) targeted milestones for sorption materials.
- The approach to focus on understanding the nature of the boron doping and its impact on enhanced hydrogen storage properties is important; however, a clear examination of the abilities of these materials to achieve DOE targets was not apparent in the results. This should be a focus of any future work.
- After many years of effort, it is disappointing to see that there are still unresolved questions regarding the most basic features of the materials, such as what the composition and local structure are.
- This project has two main objectives: (1) increase the binding energy by boron doping in the hope of operating way above cryogenic temperatures and preferably near room temperature and (2) increase the volumetric density by increasing the packing density of the activated carbon. The initial approach was plainly justified in the absence of relevant experimental results regarding these two aspects; however, the 2012 results clearly showed that boron doping does not provide a pathway for meeting the targets. The project should have been redirected in a more useful direction.
- The principal investigator (PI) does not adequately explain his approach to developing boron-doped hydrogen storage materials. In fact, not a single slide is specifically directed at the approach. While the concept is very interesting, it is based on some incorrect assumptions about the core possibilities associated with boron-doping levels in a carbon matrix (e.g., 20% brings one to boron-carbide). It is a step in the right direction that the PI is working with the National Renewable Energy Laboratory (NREL). However, a validation experiment on a single sample does not validate other past results; it validates the sample measured. The PI's later results need to be validated as well. It was very difficult to follow the talk as outlined by the PI.

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

This project was rated **1.8** for its accomplishments and progress.

- The investigators have prepared boron-doped nanoporous carbon materials with a volumetric capacity of 63 g/L and a gravimetric capacity of 12 wt.% (at 80 K). Likewise, the thermodynamic target window for enthalpy of adsorption is approximately 12 kJ/mol. The investigators show that boron-doping shifts this adsorption enthalpy to 10 kJ/mol. Both of these accomplishments are noteworthy. The foundational science is also addressed in this work. The full characterization of the boron-doped nanoporous carbons that the investigators completed using techniques such as x-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), mass spectroscopy, and Fourier transform infrared spectroscopy (FTIR) clearly guided the choice of doping strategies (e.g., deposition temperature) and could possibly give useful insight into the optimal boron content.
- Doping modestly increased the binding energy, but clearly not enough to be a pathway for meeting the DOE targets. Moreover, the doping decreases the surface area of the adsorbent and thus decreases the hydrogen uptake. The results show a modest increase in uptake by unit surface area but do not show the cost of decreasing the surface area. There should have been a go/no go point for this approach. As for increasing the packing density of the adsorbent, this is also done at the cost of decreasing the gravimetric density by decreasing surface area and also by decreasing the gas phase density which is an equally significant portion of the total storage capacity. A sensitivity analysis should have been carried out to find an optimum combination.
- Progress has been made on gaining a fundamental understanding of the boron-doped materials and the reproducibility of synthesizing materials; however, little progress has been made to show that these materials will be able to achieve DOE hydrogen storage goals. If the fundamentals of the material are still not understood, it is unclear why researchers would scale up to monoliths. Such an effort seems premature, given the uncertainties in the materials properties.
- In fiscal year (FY) 2013, there did not seem to be any significant progress toward the go/no-go metrics. The accomplishments as presented are suspect. The PI admits the presence of boron oxide but then assumes his samples have none because the experiments were performed under anaerobic conditions. However, for these syntheses, even trace amounts of water or oxygen will create an oxide impurity. Yes, there is sp^2 hybrid boron present in his samples, but the percentages are much less than assumed. The concentration variations of the monoliths were not explained adequately.

Question 3: Collaboration and coordination with other institutions

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

- The validation of measurements by NREL was an important milestone for this project.
- The PI did make an effort to work with NREL. This type of interaction should be encouraged further.
- The project lists many collaborators; except for NREL and the University of Missouri, the contributions of the others to 2012–2013 efforts are unclear.
- Although investigators list many other collaborating institutions on slide 18, the technical accomplishment slides (slides 7–13) and future work slides (slides 19–20) show primarily work done at the University of Missouri. The relationships with collaborating institutions could be further improved.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.8** for its relevance/potential impact.

- The project is relevant to the DOE storage objectives of increasing the volumetric capacity and the operating temperature of adsorption storage, among other properties.
- The project is unique in that the investigators have developed a method to “tune” the heat of adsorption using the variable of boron-doping content. This presents an exciting opportunity because the approaches

being developed in this research could be more generally applied to other nanocarbon materials to ultimately reach DOE-targeted adsorption temperatures.
- It seems unlikely that forming monoliths will improve capacity enough to significantly change the ability of the materials to achieve DOE goals.
- The presentation of data on slide 4 is disappointing. The PI made the effort to work with NREL, but then just changed the single data point. The other data in the chart were not validated, which makes the chart very misleading.

Question 5: Proposed future work

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

- The planned future work takes logical steps to overcome barriers identified during the course of ongoing research. These barriers include boron free-radical formation, oxygenation of boron doping, and "tuning" the enthalpy of hydrogen adsorption at room temperature. The future work is lacking clear plans for interaction with the collaborators listed in slide 18.
- Enough capacity data should be collected on materials with different surface areas and boron-doping levels to project what values of each would be needed to meet DOE goals.
- The proposed work may offer a little improvement of the presented results, but the developed material will be far from meeting DOE goals. A more thorough measurement of the heat of adsorption measurement is definitely warranted; clear demonstration of the advantages and disadvantages of boron doping and pelletizing is also needed to direct future efforts. Cyclability, reversibility, and reproducibility should also be demonstrated.

Project strengths:

- The project team has good knowledge of adsorption.
- The concept and verified increases in isosteric heats are an important step forward. The work with NREL is another strength.
- The validation of measurements proved the reliability of the project's data collection. Analysis of the state of the boron in the material has provided useful insight into what needs to be done to improve the materials.
- The investigators do a really nice job of characterizing the new materials. The approaches used to arrive at boron-doped nanoporous carbon hydrogen sorption materials with the potential to meet the DOE targets can be used more widely for other nanocarbons.

Project weaknesses:

- The project team is focused on improving one or two materials properties at the expense of the many others.
- It seems that most of the work is done at the University of Missouri; few results from interaction with collaborators were presented. This is a major weakness because this project relies on the fundamental characterization (offered by collaborators listed on slide 18) to guide the research to successful doping parameters (which in turn lead to useful thermodynamic properties).
- The interpretation of data: XPS, monolith, and densities is an area of weakness. There is boron oxide in the samples. Until the PI acknowledges and takes this data point into consideration, the interpretation of the data is incomplete.
- The presenter did not fully address the reviewer statement that not a lot of progress has been made in improving capacity; instead, the presenter pointed to efforts to validate measurements and improve reproducibility in production. So two years have passed without significant improvement in materials properties. While the data has been validated by measurements at NREL, the validity of methods to determine ΔH (enthalpy change) should also be addressed. With isotherms measured at only two closely spaced temperatures, and depending on the method of determining absolute capacity, the margin of error may be quite large.

Recommendations for additions/deletions to project scope:

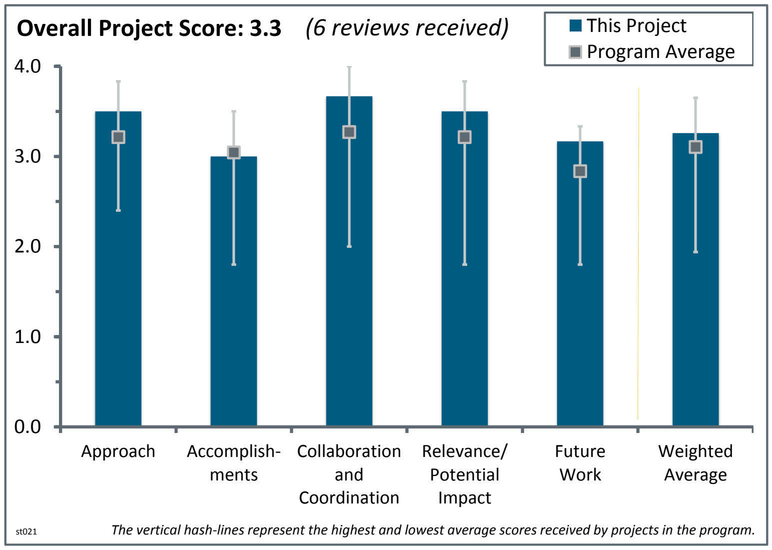
- This project should be discontinued.
- The researchers should add a go/no-go decision point after optimizing the doping of granular material. They should also measure reversibility and demonstrate cyclability and reproducibility. Using the current data, it should be possible to project how much capacity improvement can be achieved by compaction into monoliths. If the projections do not show that compaction provides a clear path to capacity goals, then the work on monoliths should stop.

Project # ST-021: Weak Chemisorption Validation

Thomas Gennett; National Renewable Energy Laboratory

Brief Summary of Project:

This project evaluates the spillover process for hydrogen storage on metal-doped carbon materials. The objectives of this project are to: (1) validate measurement methods, (2) identify and synthesize several candidate sorbents for spillover, (3) determine hydrogen sorption capacity enhancement from spillover, and (4) observe and characterize spillover hydrogen-substrate interactions with spectroscopic techniques. The project will validate observations for a narrow range of spillover material systems and will synthesize and distribute targeted materials for group analysis.



Question 1: Approach to performing the work

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

- This project features an excellent approach designed to answer the question of whether or not there is significant spillover hydrogen storage at room temperature.
- The project team performed a very thorough analysis.
- The National Renewable Energy Laboratory (NREL) has demonstrated a good, disciplined approach to evaluate and demonstrate the "spillover" mechanism.
- The round-robin synthesis and measurement effort is an outstanding step toward the validation of hydrogen sorption capacity enhancement from spillover.
- The goal is to use a range of experimental methods to validate the role of spillover in physisorption systems that use metal-doped carbon. The experimental work is first rate and the researchers have developed a team to validate whether the effect is real. They have demonstrated that the effect is real with the determination of a carbon-hydrogen bond. There is no discussion of the weight percent enhancement. There is no discussion if all of the hydrogen comes back off and how often one can cycle the system. It is unclear if the spillover sites get blocked.
- The intent of this project was to clarify via cooperative and definitive experimental studies whether the widely touted hydrogen spillover mechanism could actually produce greatly enhanced hydrogen storage capacities of carbon adsorbents with properties conducive to meeting U.S. Department of Energy (DOE) hydrogen storage performance targets. The approach was to characterize shared samples with metal additives that reportedly exhibited at least 15% higher capacities at ambient temperature due to hydrogen spillover. Measurements were done in different laboratories and supplemented with spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR), neutron vibrational spectroscopy (NVS), and nuclear magnetic resonance spectroscopy (NMR).

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

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

- The project has accomplished the specified goals and completed the necessary steps to confirm the existence of the "spillover" mechanism.

- Many techniques have been developed out of this project; using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for the direct evidence of carbon-hydrogen interaction is a particularly great achievement.
- This project has definitely established that large amounts of hydrogen storage (e.g., 4 wt.%) do not occur at room temperature.
- The researchers have made excellent progress in reconciling the mechanism of metal mediated processes with different substrate matrices. The first direct spectroscopic evidence of a reversible room temperature sorption/desorption were apparently from a unique carbon-hydrogen interaction via DRIFTS, NMR, and neutron scattering spectroscopy techniques. Researchers validated results by using different groups to make the measurements. It is unclear what wt.% the researchers think they can get at what temperature. The project team demonstrated the need for more fundamental work in the area and showed the need for very careful experimental work. The team did not show what other metals might be practical or connect to other work in catalysis where the amount of hydrogen on iridium doped in a zeolite has been studied.
- Overall, this project has attained its goals. It would be preferred if this project would progress somewhat faster, but measuring such a small effect (as appears to be the case for spillover) is a non-trivial task.
- After nearly three years of effort by the various partners in this project, modest (i.e., circa 15%–30%) capacity increases can be attributed to hydrogen-spillover from metals such as platinum, palladium, and ruthenium on lower surface area carbons. Evidence for some hydrogen-carbon chemical bonding is indicated via FTIR and NMR; however, facile reversibility as required for practical storage applications was not found. While the spectroscopic techniques provided complementary information on the presence of hydrogen-carbon bonds, a comprehensive description of the spillover mechanism has yet to be presented.

Question 3: Collaboration and coordination with other institutions

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

- A large number of collaborating groups are working together on this project—each bringing its own expertise—making it a great, coordinated effort.
- The team’s excellent collaboration helped demonstrate the effect. There were 4 groups focused on spillover and 11 groups on measurements. The project featured very good teamwork and is to be commended. Such a team approach is needed to determine if the effect is real or not.
- The collaboration on this project seems to be very good because they attempted to coordinate with many of the researchers in this field.
- Besides NREL, both domestic and international research groups with experience and expertise actively participated in producing test materials and conducting volumetric hydrogen capacity and spectroscopic measurements. However, subcontracting and other issues delayed the round-robin testing that ultimately reduced the time available to conduct the critically required experiments.
- It is curious that there was no collaboration with Ralph Yang at the University of Michigan.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The evaluation of the spillover approach as a means to achieve DOE goals is very important for the overall objectives.
- This project provided a very important validation service to the DOE Hydrogen and Fuel Cells Program; it essentially “closes the book” on spillover.
- The project has significant relevance because it confirmed the “spillover” mechanism to the hydrogen storage research community. However, the initial impact or contribution of “spillover” to improving materials toward the desired storage goals at room temperature appears to be much less than previously predicted.
- The work shows the presence of a spillover effect. This is not unexpected based on the catalysis work, but it is nice to demonstrate that it is there. There did not appear to be any quantification of how much more hydrogen is stored and what the reversibility/cycling time is. It is unclear if all of the hydrogen comes back

off and for how many cycles this can be repeated. There is no discussion of the potential use of cheaper metals and what the next steps should be other than that more basic science studies are needed. Perhaps it can be made practical.
- It would certainly be important if the spillover phenomena could produce significant room temperature hydrogen storage. Sadly, this does not appear to be the case.
- The results generated during this project suggest that some positive impacts can be had from a hydrogen spillover process with selected metals. In particular, clear indication for the formation of carbon-hydrogen bonds has been demonstrated. However, the levels of storage enhancements are much too modest to be effective for meeting DOE performance targets.

Question 5: Proposed future work

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

- The project has completed its goals and no significant future work remains.
- The proposed future work appears to be appropriate, especially in the determination of the ultimate spillover capacity possible once researchers completely establish/optimize the interactions and substrate chemistry.
- The ultimate spillover capacity needs to be determined under practical tank operating conditions; this is not included in the future work.
- The project is essentially complete. It would have been good to have seen a bit more on what is really needed to make this a useful storage system.
- The project is nearly over. The most important last order of business is to determine the ultimate spillover capacity possible.
- This project is nearly completed, with only one or two experimental tasks (e.g., NMR measurements under hydrogen pressure on perhaps one more sample) remaining at the time of the DOE Hydrogen and Fuel Cells Program Annual Merit Review. It would be most helpful if the principal investigator and his partners could prepare a comprehensive final report/paper fully describing their samples, detailed characterizations, observations, and whatever conclusions can be drawn either supporting or debunking the hydrogen spillover process. In particular, the challenges of performing reliable and robust measurements should be fully reported, including insights on technical difficulties and inconsistencies encountered during the study.

Project strengths:

- This project features a strong team and experimental approaches.
- This project features a highly qualified team.
- A large number of collaborating groups are working together on this project—each bringing its own expertise—making it a great, coordinated effort.
- This project features excellent, high-quality experimental work. Other strengths include the excellent team approach to demonstrating the phenomenon and the very careful measurements.
- The project included various levels of supporters and skeptics to develop the assessment of the “spillover” mechanism.
- The involvement of diverse groups with qualified researchers to assess this contentious issue is appreciated. The intent of performing independent experiments on common samples with clearly specified handling and test protocols is clearly a very desirable aspect of this project.

Project weaknesses:

- The real tank operating conditions need to be included under the evaluation of the spillover approach.
- The slowness of providing funding and samples for study probably limited the time to perform the actual experiments necessary. There are still unresolved issues with slow kinetics for hydrogen on the carbon substrate and oxygen/hydroxyl contaminations.
- There was no discussion of actual weight improvements. Other weaknesses include the lack of discussion about the following: the future for spillover; cheaper, lighter metals; how big the metal particle is; and what doping levels are needed to be an effective hydrogen material.

Recommendations for additions/deletions to project scope:

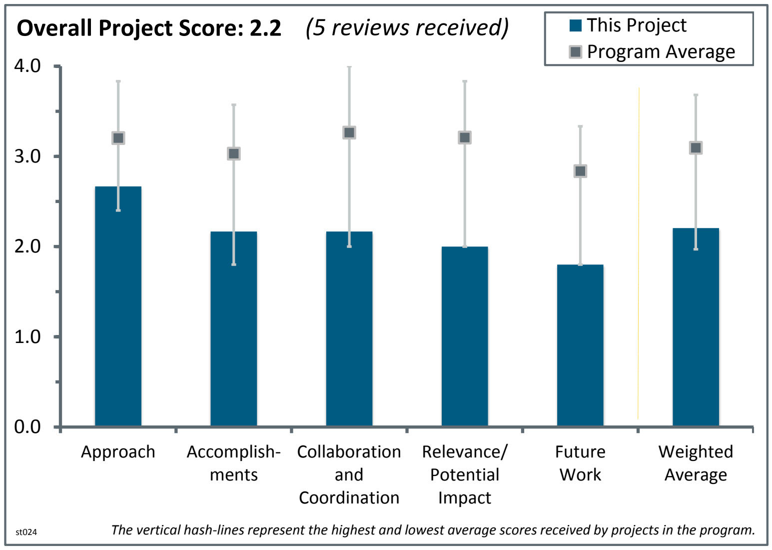
- It will be very important for this project to assess the potential of "spillover" before completion.
- This project is essentially complete. The researchers should finish the project and provide input on future directions for spillover studies.
- There are no recommendations because this project is nearly complete.

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 primary objective of this project is to synthesize designer microporous metal-organic frameworks (MMOFs). The project focuses on synthesis and optimization of one catalyst-doped MMOF, addressing gravimetric capacity, delivery temperature, kinetics, and reproducibility. The goal of the research is to demonstrate the full potential for hydrogenating a MMOF.



Question 1: Approach to performing the work

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

- The focus on attempting to show spillover in the best potential metal-organic framework (MOF) material was good.
- A rational approach is outlined and followed. Researchers have identified a particularly robust MOF that can be catalyzed and apparently remain crystalline. The efforts to identify and focus on one material have helped define the project.
- The primary objective of this project at Pennsylvania State University (PSU) is to discover and characterize specific carbon materials, namely MOF compounds, where hydrogen spillover processes from metal catalysts can give reversible hydrogen storage of several weight percent at ambient temperature. If this capacity can be verified, spillover effects may give a pathway to materials that would approach the U.S. Department of Energy (DOE) targets for passenger vehicles. A fiscal year (FY) 2013 milestone was to demonstrate at least a 3 wt.% reversible storage capacity near ambient temperature with acceptable kinetics. While the original approach was to synthesize promising MOFs then add metallic catalysts to confirm enhanced storage via volumetric and gravimetric experiments, extensive spectroscopic studies have been made to look for a hydrogen-carbon bond via spillover. Complementary first-principles calculations have been used to examine both thermodynamic and kinetic factors that either permit or inhibit the desired reversible reactions.
- The general approach is OK, but it needed to focus more on the practical hydrogen storage tank operation condition.
- When combined with the National Renewable Energy Laboratory (NREL) results, this study shows that spillover is not going to lead to even moderate uptake at room temperature and is rather difficult to measure.
- It is unclear why the project team thinks the chosen catalysts will perform better than those explored previously by other researchers.

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

This project was rated **2.2** for its accomplishments and progress.

- The robust pre-bridge (PB) doping technique is very interesting and could have impact on other materials. However, the measurement must be focused on the high pressure. It would be a great achievement for the

hydrogen storage community if the principal investigator (PI) can demonstrate whether the spillover approach can or cannot achieve DOE goals based on the real measurement.

- If DFT calculations indicate that one can hydrogenate a substrate, it is unclear how that is evidence of reversibility. The hydrogenation is exothermic—the reserve is quite endothermic and not reversible.
- The project has shown a small increase in spillover hydrogen storage in MOFs, but only 1% hydrogen storage at room temperature. The project could not meet the go/no-go decision point criteria.
- Progress has been somewhat limited, mainly due to the difficulty in measuring spillover. To some degree, this is not the fault of the PIs.
- After investigating a series of MOFs with additives of microscopically dispersed platinum particles that would allow the hydrogen spillover process to take place where its laboratory tests did not reproducibly show enhanced capacities, PSU chose to concentrate on a single promising MOF-platinum combination. While initial low-pressure measurements suggested there could be substantial spillover effects, only limited enhancement (e.g., <1 wt.%) was seen at higher pressure where extremely slow reaction kinetics were also observed. Hence, PSU has failed to meet its go/no-go target. PSU continued to revisit and adapt its techniques for measuring hydrogen capacities in order to improve accuracy and reproducibility. PSU has decreased errors, but it did not verify past reports of room temperature capacities greater than ~1 wt.% nor did it achieve acceptable reproducibility. Raman and other spectroscopic data do suggest some hydrogenation does occur that may be associated with the spillover processes, although data interpretations are still rather controversial.
- Some improvements over native materials may be apparent, but given the 50% to 100% variability between batch and/or run, the magnitude for a typical bulk sample is uncertain. Additionally, reviewers were not told the timescale for these low-pressure uptakes; it is unclear if they are at equilibrium or for the 20-hour exposures. Surface diffusivities seem to be dominant and no clear connection between material stability and diffusion activation energy has been presented to see if these barriers can be reduced. MOF-nitrogen is not described or referenced, so most of the results to do with spectroscopy cannot be interpreted independently and reviewers must rely on the stated results. From slide 14, it is unclear if reviewers are to believe that this is a $Cu\text{-}O_2$ linkage at the metal. The difference between the MOF-nitrogen and PB-MOF-nitrogen shows a significant amount of reduced $Cu\text{-}O_2$ in the prepared sample that is further reduced and somehow partially reversible. There are no indicators of this being handling, sample-position, or sample batch dependent—this is something worth testing in this context. On slide 16, it seems that there has been some effect on 300 K, 70-bar hydrogen exposure: the lowest angle peak, broadened peaks, and the greatly reduced intensity with scattering angle indicates partial degradation—much the same as in the PB-MOF-nitrogen case, and further accentuated in the hot hydrogen plot. This might not be stable in the long term and needs to be tested.

Question 3: Collaboration and coordination with other institutions

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

- The project features reasonable collaborative interactions.
- Some helpful collaboration was evident with projects outside of the DOE Office of Energy Efficiency and Renewable Energy (EERE).
- PSU continues to collaborate with the co-PI at Rutgers University (RU), who is synthesizing different MOFs with properties for potentially greater hydrogen capacities. There have been interactions with several other researchers on characterizing samples and looking to verify reproducibility of the capacity measurements. A strong theoretical relationship is evident with the University of Crete.
- The PI should coordinate more with NREL's team and utilize its expertise in this work, since the scopes of the projects are similar.
- It is not clear whether there were candid discussions between the collaborators about spillover and why the project has received a no-go decision in 2013.
- The presentation did not detail any significant collaborations besides obtaining MOFs from RU and independently funding modeling work at the University of Crete.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.0** for its relevance/potential impact.

- The project is relevant, but the potential impact is low due to the limited benefits of spillover.
- Even if the spillover concept works, the high cost and low density of the selected material will not likely meet the overall DOE objectives.
- There has not been convincing data supporting the “reversible” spillover mechanism in prior years and this presentation does not change that.
- Achieving significant hydrogen storage near room temperature would have a major impact. Alas, this does not appear to be possible via the spillover approach.
- Hydrogen spillover involving platinum-catalyzed MOFs to sufficiently enhance the storage capacities to meet the DOE targets does not appear to be a viable pathway. Not only is there minimal additional hydrogen storage, but the kinetics are atrocious. The results of the recent modeling are not really encouraging. There seems to be little potential for such hydrogen spillover processes to contribute to meeting practical hydrogen storage in any application.
- As identified by the PI, there is little hope for spillover being useful within the scope of EERE goals until fundamental spillover knowledge is gained. Even then, using relatively heavy MOFs as a spillover target will never meet the hydrogen loading levels needed to achieve DOE’s goals. Uptakes of catalyst-bridged species up to 0.04 wt.% at 1 bar and between 0.3 and 0.6 wt.% at 70 bar are practically meaningless compared to the DOE targets. For activated carbons, the final capacity has to be almost one hydrogen per two carbons, so it is unthinkable to achieve this with the weight penalties of metals in these hybrids. However, a bullet point indicates that 3.5 wt.% may be possible from a calculation (no details were given).

Question 5: Proposed future work

This project was rated **1.8** for its proposed future work.

- The project is essentially over. A no-cost extension to allow the students to finish has been requested.
- This question is not applicable. The project is ending.
- There are no direct, high-pressure measurements planned in the future work.
- Rather than performing DFT calculations, the project team should collaborate with an experienced theoretician who can pick the modeling methodology.
- The current work raises more questions than it solves. These should be addressed by peer review prior to embarking on a new series of materials properties that require further doping to potentially enhance diffusion rates.
- The plans shown on slide 21 for completing preparation and characterization of modified MOFs are reasonable if they can be accomplished within the current funding levels. This project will miss its revised go/no-go decision point of demonstrating 3 wt.% hydrogen capacity at “moderate” temperatures in FY 2013. Based on results obtained by the team to date, this goal is probably not achievable using currently investigated materials and treatments.

Project strengths:

- This is a valiant attempt to demonstrate room temperature H_2 storage in MOFs via the spillover approach.
- The isotherms for “spillover” type materials are better than the water-generating initially high uptakes of previous years.
- PSU undertook a committed effort to improve the accuracy of its methods for measuring storage capacities that included interactions with other organizations. It has revisited issues of doping materials and looked for more promising candidates to be studied. The use of various spectroscopic methods has been insightful and worthy of praise.

- This project provides the hydrogen storage community with some fundamental understanding of how the spillover concept works. The team also developed some robust doping techniques that can be used for other materials.

Project weaknesses:

- The measurement is not focused on the high pressure. It would be a great achievement for the hydrogen storage community if the PI can demonstrate whether the spillover approach can or cannot achieve DOE's goals based on the real measurement.
- Reproducible and accurate measurements of hydrogen storage capacities remain a major challenge with small samples. Apparently, the processes and procedures used both to prepare the MOFs and to incorporate the catalysts remain difficult and still lead to irreproducible measurements. The very slow kinetics for the transfer of hydrogen during the spillover process remain a very serious issue, even if slightly greater capacities are demonstrated compared to undoped samples. The idealized conceptual mechanisms for hydrogen spillover are apparently greatly oversimplified and unrealistic. While first-principles calculations might be helpful using graphene surfaces for MOFs and other carbons, transference of these predictions can also be highly misleading. This phenomenon has been greatly oversold to the hydrogen energy community as a way to meet hydrogen storage performance targets.
- This project does not help to resolve uncertainty in the spillover field. It is clear from the NREL-led project (ST-021) that spillover is small and frequently difficult to reproduce for many systems. Worthy of consideration, however, is that according to the presentation of Gennett (ST-021), the opinion of a dozen or more researchers, apparently including this PI, is that it would be impractical for DOE to continue R&D on spillover at this time. It is unclear how the resources were spent, including for a co-PI who seemed to provide limited contributions to the project's goals. All of the units on the uptake graphs should be the same. Publications are limited—they are mostly from 2011, with one published in 2013 and one submitted.

Recommendations for additions/deletions to project scope:

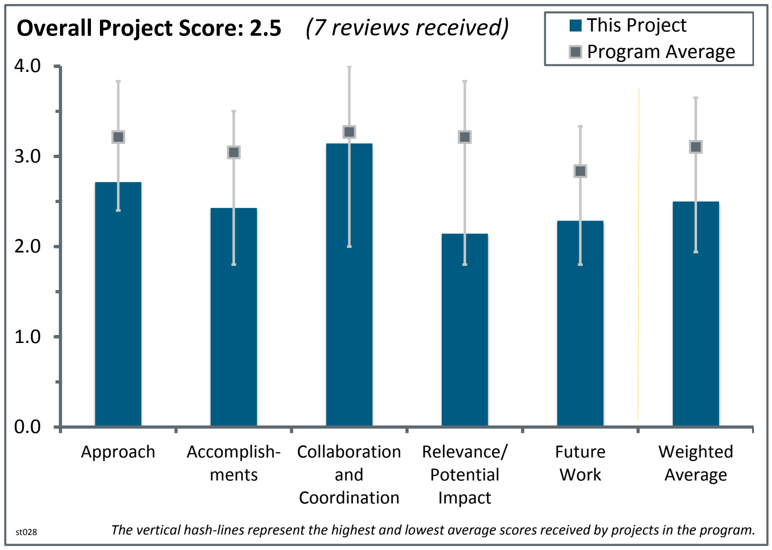
- The PSU/RU team has failed to meet its FY 2013 capacity target and should not receive additional funding from DOE. However, a no-cost extension of the contract would be desirable to complete publication of the results/analyses and to allow students to finish their theses. It seems unclear whether additional work on these systems is warranted due to the myriad issues with reproducibility, very bad kinetics, and minimal evidence for reversibility.

Project # ST-028: Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

Christopher Wolverton; Northwestern University

Brief Summary of Project:

This project studies combinations of materials to form novel multicomponent reactions. The research includes hydrogen storage measurements for automotive applications, computational prediction of novel reactions, and kinetics/catalysis/ synthesis experiments. Efforts in the past year were focused on two main reactions predicted to have high capacity and suitable thermodynamics for hydrogen storage applications: $2LiBH_4$ + $5Mg(BH_4)_2$ and $B_{20}H_{16}$.



Question 1: Approach to performing the work

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

- The approach is excellent and involves complementary methods: experimental measurements, characterization, and computational modeling. The researchers compared pure chemicals, composites, and catalyzed systems, and they have a strong focus toward well-defined automotive applications.
- This project is sharply focused on critical barriers; it is difficult to improve the approach significantly. The project is well designed to address some of the key barriers. It is nice to see that the project is focused on a few of the most promising reactions obtained from computational screening. The computational efforts seem well integrated with the experiments.
- This joint project of Northwestern University (NWU); the University of California, Los Angeles (UCLA); and Ford Motor Company involves a combination of first-principles calculations (NWU and UCLA) of candidate hydrides and their structures along with predicted reaction pathways. The goal is to identify mixed component hydrides with potentially sufficiently large storage capacities that might meet U.S. Department of Energy (DOE) targets for passenger vehicles. Over the past couple of years, the emphasis has been on the role of defects that can underlie diffusion processes with implications for a better understanding of the kinetics. Experiments are being used to determine the as-prepared and decomposition phases in order to ascertain reaction pathways. Solid-state nuclear magnetic resonance (SSNMR) experiments were utilized to identify “amorphous” components in desorbed borohydrides to complement past characterizations. The team has also looked at catalysts to enhance the kinetics. The objectives generally comply with the DOE targets and goals.
- There were significant changes apparent in the project from the previous year, with more focus and outside expertise to assist in the experimental work. The project has obvious strengths in computational expertise but is still lacking on the experimental side. This is a surprise given the reputation of the experimental co-principal investigator (PI) and makes one wonder if the project team is involved at an engaging level of interest.
- The approach may have some impact on the understanding of the diffusion of species in complex metal hydrides. The team may not have the best makeup to take advantage of this because the diffusion modeling then calls for diffusion studies by nuclear magnetic resonance (NMR) and or quasi-elastic neutron scattering (or other appropriate techniques relevant to the diffusion time scales) to confirm the modeling results. The approach could be sharpened by not investing more resources in combing over systems looked at extensively by the Metal Hydride Center of Excellence unless it can be justified via new observations or modeling insights. The approach could be improved by reconciling the current project with information

from the literature. The approach included the addition of an SSNMR capability this year, and it was good to see the project respond to suggestions from various reviewers. The approach included the synthesis of the difficult $B_{20}H_{16}$; it is unclear whether the theoretical modeling result truly justifies the effort because the synthetic thermal chemistry route appears to include $B_{10}H_{14}$ as a required reagent that does not appear to be accounted for in the modeling result.

- This project needs more of a balance between experimental and computational work. Additional experimental work was added this year but it appeared too late in the overall project plan.
  There is no real link between theory and experiment in the project. The simulations are what are easy for the researchers to do, not what is relevant to the hydrogen storage problem. Their approach can only deal with diffusion in essentially idealized materials with possibly some defect sites. They cannot readily study the hydrogen release mechanism from the actual compounds because their solid-state DFT approach does not work well for this and they do not know what the various intermediates are. They have not looked at the costs of the materials. They propose to make $B_{20}H_{16}$ (icosaborane-16) with Dr. Shore at The Ohio State University (OSU), yet the starting materials cost is approximately \$50/g, so 1 kg costs around \$50,000; although, one might be able to get close to 1 kg for \$10,000–\$15,000. The process to make $B_{20}H_{16}$ might result in a yield of only 10%, thus the cost of the $B_{20}H_{16}$ is likely on the order of \$100,000–\$500,000/kg. This is not practical in terms of cost for a hydrogen storage system and makes this work completely irrelevant. If instead the researchers started with pure boron as the product, the rehydrogenation cost would be around \$100,000 for 1 kg. This is not feasible because the material would have to be remade each time. There is a lack of understanding of cost and practical engineering issues with the proposed work. Since most of the computationally determined compounds have not been reversible or are unable to be synthesized, there is little practical value of the work. Production of BN and boron by-products can give a reasonably high weight percent, but the products cannot be readily regenerated so it is all useless effort. There is nothing relevant being proposed here at all. The team appears to be unaware of the work on $(B_{12}H_{12})^{2-}$ complexes with NH_4^+ in the literature for hydrogen storage purposes. One has to be careful of calculating the energetics on a per mole of hydrogen basis because this does not really show what is happening. There can be very high-energy steps that may make the overall thermodynamics irrelevant in terms of kinetic issues because these high-energy intermediates may need to be coupled with low-energy ones to get hydrogen released at a reasonable temperature. The team could not find such intermediates with its computational approach and has not accomplished it with its experimental team, either.

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

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

- There has been progress toward meeting objectives and overcoming barriers. Three of the more promising reactions (determined from an earlier screening effort) were investigated. The predicted thermodyamics for $B_{20}H_{16}$ look good. The study focused on kinetics, specifically mass transport. The synthesis of $B_{20}H_{16}$ with OSU is showing limited progress with low yield. Hopefully, $B_{20}H_{16}$ can be isolated/purified for further experimental studies. The NMR work on $LiBH_4$ and $Mg(BH_4)_2$ shows an indication of B_2H_6 being present, as predicted computationally—that is a nice synergy between experiment and theory.
- Efforts to better model the hydrogen transport processes in prototype B-based hydrogen storage systems have continued over the past year and have suggested that $B_{20}H_{16}$ might have properties amenable to improved storage behavior. The first-principles calculations of defect energies and diffusion parameters clearly show that kinetic barriers generally impede the performance of B-containing phases—even if thermodynamic properties are improved by using a combination of hydrides. NMR measurements suggest that most past speculations on decomposition reactions and products are inconsistent with experimental observations. Further investigations will be needed to unravel the actual mechanisms. Many challenges remain in the development of hydrides that can meet DOE's performance targets.
- The productivity of the theoretical modeling work appears to be good; the experimental aspects of the work seem to be lagging behind. The NMR effort appears to have come up to speed fairly quickly and is providing good feedback to the materials effort. There was little evidence of researchers reconciling data from the literature with their own results, which would be helpful to put their accomplishments into perspective.

- The research is focused on light element hydrides with high theoretical hydrogen capacity. A major part of the experimental measurement appears to investigate moderate temperatures, which is also very good. In some cases, some reversible hydrogen storage capacity is observed, and catalytic additives clearly have a positive effect. In particular, for the system $2LiBH_4$-$5Mg(BH_4)_2$, it may be only Mg/MgH_2 that stores hydrogen reversibly under the chosen physical conditions.
- Very little experimental work was done on $B_{20}H_{16}$, which was identified as “extremely promising.” More experimental results should have been shown for this material.
- The researchers have done bits and pieces without looking at the overall system. The computational work is simple in terms of the diffusion studies, but more is needed. Their tools do not provide the proper chemical insight into the mechanism and the experimental component is not focused on determining/understanding the mechanism. Their computational energetic results provide minimal insight into the actual energetic or kinetics of the real processes. A global mechanism here is of little value. The cost issue has not been addressed.
- Regarding the $B_{20}H_{16}$ project, the reason why the research team does not spend some time on the “reverse reaction” is unknown; perhaps the PI explained it at the 2012 DOE Hydrogen and Fuel Cells Annual Merit Review. It seems that if the reactions of interest are reversible, the research team could start on both ends and work toward a common middle ground. Perhaps it would be more direct to start with “20B”boron and hydrogen under pressure to make the more stable product $B_{20}H_{16}$. It could save significant time and effort in making the $B_{20}H_{16}$. The good news is the $B_{20}H_{16}$ is stable, slightly hygroscopic, and apparently nonflammable. However, the bad news is that it is likely to be too stable. Melting occurs at 196°C without decomposition. It would appear that the kinetic barriers leading to hydrogen release are significantly higher than the diffusion barriers. It is great that the researchers have approached Dr. Shore and his group at OSU to make the material, but it is unclear if they also asked Dr. Shore his opinion on how this complex would decompose. It is good that the PI has observed a decrease in hydrogen release temperature by adding 10% product to the $Mg(NH_2)_2$-LiH mixture; however, it is unclear how “seeding” the $B_{20}H_{16}$ with boron would make a significant difference in the decomposition. It is unclear if there is a scientific basis for this or if it is just hopeful thinking. It would be beneficial to have a mechanistic idea of when and how the product leads to decomposition in the hydrogen release temperature. It is possible that an impurity of any type could lower the melting point and the decomposition could be enhanced in the liquid state. However, it is unclear how general this observation is and how “profound” it really is. Decreasing the onset decomposition from 200°C to 80°C is asking a lot. For the BH_4 project, the PI is commended for bringing in expertise in NMR spectroscopy. The researchers provide a good start toward interpreting the NMR results, but it is quite likely that the broad peak at 26 ppm is a complex mixture of products. It is unclear if there is some rationale that would explain why one species is so broad and the other species is narrower. The Yan paper in “Mater Trans” (Mat. Trans. [2011] 52:1443-1446) could not be readily obtained to discover if it was an experimental or computational paper. However, Dr. Chong and her co-workers at the University of Hawaii at Manoa collected both solid-state NMR and solution NMR for the decomposition products of magnesium borohydride decomposition. Based on the early literature of Hawthorn, Shore, and others, the researchers described a BH condensation decomposition pathway of BH_4 followed by a multi-step reaction involving several B_xH_y (X = 1–12) intermediates, and that the broad signal observed in the solid-state spectra is most likely due to a wide range of products, not just one or two species. It is unclear if there is some scientific explanation for a change in reaction mechanism for neat magnesium borohydride to the mixture proposed here. Without access to the Yan paper, it was difficult to know what the paper described. The researchers’ admitted surprise that they observed a B5 species prior to a B2 species, leading them to believe there are other explanations and a more complex reaction scheme. It is unclear how the calculated NMR shifts compare with the observed chemical shifts. It is unclear if the NWU researchers have shared the ^{11}B NMR data with Dr. Shore and asked his opinion on the product assignments. It could be very helpful to obtain the mass spectrum of the decomposition products. This would be a more certain lock on product identity, whereas the NMR can only provide an ambiguous result.

Question 3: Collaboration and coordination with other institutions

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

- Excellent interaction was indicated between the theoretical members of this team. The addition of the NMR measurement and borane synthesis researchers was a definite improvement.

- This project features well-coordinated collaboration with the California Institute of Technology (Caltech), Ford, and OSU.
- The project appears to be very well coordinated. The number of partners and collaborators is appropriate compared to the amount of funding available.
- The additions of Caltech and OSU were good additions to this project since last year.
- The teaming with Dr. Hwang at Caltech for NMR is great. He is one of the best at collecting solid-state spectra. The teaming with Dr. Shore is also great. The researchers need to talk to Dr. Shore more about the chemistry and NMR data collected by Dr. Hwang. The team members deserve a rating of "outstanding," but less than outstanding for getting the new subcontractors more involved in analysis and interpretation.
- The team is lauded for incorporating the SSNMR capability and was thus responsive to reviewers' comments from the previous year. Collaboration between experimental efforts and the modeling effort could be tightened up with better mechanisms for feedback. Collaboration from outside of the project could help this team better approach some of the observations it is making in the $LiBH_4$ and $Mg(BH_4)_2$ systems.
- The internal collaboration of the team members is good, but no details were provided on the roles of the external collaborations or even about what the UCLA or Ford groups are doing. The focus is on the computational work at NWU. Working with Dr. Shore at Ohio State is good.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.1** for its relevance/potential impact.

- Most project aspects align with the DOE Hydrogen and Fuel Cells Program and DOE RD&D objectives. Like many other projects, the potential impact is high, but the likelihood of success is probably pretty low. In these cases (when no high-capacity reversible hydride is discovered), the value comes from the publications and other documentation that will allow others to build on this work.
- The work conducted in this project is of high quality and relevant to the Program. There is a strong focus on thermodynamically stable compounds. However, the kinetic properties for composites are equally relevant and important. Therefore, the composites investigated in this project may be those that are not useful for reversible hydrogen storage because the decomposed reaction product is a very thermodynamically stable compound.
- This project partially supported the Program by identifying some new candidate materials by computational methods, but not enough experimental work was performed to validate the models and assumptions.
- Understanding transport within these complex materials is an important aspect of this work and can indirectly lead to approaches that address certain current barriers to hydrogen storage in complex metal hydrides. The project's impact would be improved if there were some experimental feedback of diffusion rate measurements into the modeling effort. The impact could also be improved by better integration of theory effort with the experimental effort.
- There is a serious disconnect between the kinetics of diffusion and the kinetics of bond breaking. The defect and diffusion calculations may be useful for some chemical transformation, but if the B_{20} does not decompose at 200°C, this is a strong indication that bond breaking and bond making are the rate-limiting steps. It is not trivial to calculate the kinetic barriers. First, one needs to know the key intermediates, and it is not apparent that this group is identifying the key intermediates unless it gets more involvement from Dr. Shore.
- Some potentially attractive candidate reactions have been theoretically predicted and their thermodynamics and defect properties were at least partially verified by testing or other analyses, but none exhibit the highly desirable reversibility behavior at moderate conditions. The work on the $LiBH_4$-$Mg(BH_4)_2$ phases appears to show much of the same behavior found and published by other research groups over the past couple of years. It seems that none of the hydride phases or compositions evaluated will be acceptable for most hydrogen storage applications.
- The cost of 1 kg of material of interest is at least $100,000–$500,000 per kilogram—this makes these materials somewhat impractical. In addition, the regeneration cost would most likely be the same if not more than that for the starting material. There is no discussion of the issues with sold-state materials. Also, there is no consideration of the regeneration costs or issues.

Question 5: Proposed future work

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

- The further experimental studies of different catalysts appear to be very promising.
- The emphasis on completing the synthesis and characterization of $B_{20}H_{16}$ should be a top priority.
- Plans build on past progress and generally address overcoming barriers. Synthesis and characterization of a pure phase of $B_{20}H_{16}$ should be completed before the project ends next year. Hopefully, the synthesis will be completed in time to allow for sufficient characterization. The computational efforts to find low-lying eutectics look interesting.
- NMR is a good start, but mass spectroscopy would provide more detail about the complexity of the products. High-resolution EI , CI, or Maldi approaches should be investigated. NWU must have some very good mass spectroscopy facilities and expertise. It is unclear if there is a good reason that the team does not start with a mixture of $Li_2B_{12}H_{12}$ and MgH_2 and pressurize with hydrogen to learn if the reaction is indeed reversible. The same can be suggested for the $B_{20}H_{16}$ if the products are boron and hydrogen. The team should do the reverse reaction first. All of these reagents are readily available and do not require complex synthetic reaction schemes.
- Future experimental work includes three materials: $B_{20}H_{16}$, the LiBMgH system, and $LiBH_4$/carbon. This appears to be a considerable dilution of effort on the experimental side. Perhaps the team should focus on two of the three. Alternatively, the team should plan on a cursory examination of $B_{20}H_{16}$ because it does not sound like the project is going to get its hands on a lot of this material. If hydrogen release is slow or yields a significant number of BH end products, then perhaps the team should look at where the modeling went awry, but then focus on the two remaining systems. The team should fail fast and move on to more promising systems.
- Because this project will end within a few months without a no-cost extension or new funding, it is unlikely that all of the planned tasks shown on slide 26 can be performed, let alone completed. However, continuing the theoretical modeling of the behavior of the $B_{20}H_{16}$ along with its synthesis and properties assessment seems worthwhile. In a short period, researchers can also probably look into the reversibility of the LiBMgH system, including hydrides within carbon composites via NMR, and model the diffusion parameters of eutectic phases of borohydrides for which there are recent results in the literature.
  The researchers need to focus on chemical mechanisms and on cost. This is not in their plans.

Project strengths:

- This project’s strength is its computational expertise.
- This project features excellent synergy between theory and experiments. The project is well focused on the most promising reactions. There are well-coordinated collaborations.
- The PI has good computational skills and a reasonable knowledge of hydrogen storage phenomena. Adding NMR and material synthesis at the request of last year’s review was favorable.
- This project features a strong team with background in materials, boron chemistry, theory, and SSNMR. This strength could be improved by adding an experienced complex metal hydrides experimentalist.
- The two theoretical groups at NWU and UCLA have developed very insightful and effective computation procedures for performing the prediction and modeling of potential storage materials. The involvement of qualified researchers for preparation of novel borane compounds (OSU) and solid-state NMR measurements (Caltech) to this project added increased capability to the experimental scope.
- This project has no strengths—the material is irrelevant in terms of cost and the researchers are not pursuing the important issues.

Project weaknesses:

- The synthesis of $B_{20}H_{16}$ seems slow.
- This project suffered from a lack of adequate experimental activities.
- This project involves a good experimentalist, but it is not apparent that the experimentalist and the team are having critical conversations.

- This project features a lack of strength in complex metal hydrides experiments. Researchers could improve the project by reconciling project results with other existing research results in a convincing manner.
- Most hydrogen desorption behavior observed in this project during the experimental studies was for materials with limited or no reversibility. These are unlikely candidates for nearly all applications. Unfortunately, connecting first-principles calculations of defect formation and migration barriers often involves convoluted routes to establish reaction pathways and kinetics because numerous other more likely rate-determining processes are neglected. It appears that Ford played a much smaller role in this project during the past year than previously.
- The computational work should focus on the release kinetics, not on hydrogen transport in an idealized material. They also need to focus on materials that have practical costs.
- The utilization of catalysts/additives clearly has a positive effect, but it is not yet clear whether this effect is purely kinetic or whether it involves a change in mechanism. Simulations have suggested a range of meta stable magnesium borohydrides. It would be desirable to have more experimental data that could support the existence of some of these boranes, although that is extremely challenging. The team should also consider utilizing Raman spectroscopy for identification of the higher borane samples produced.

Recommendations for additions/deletions to project scope:

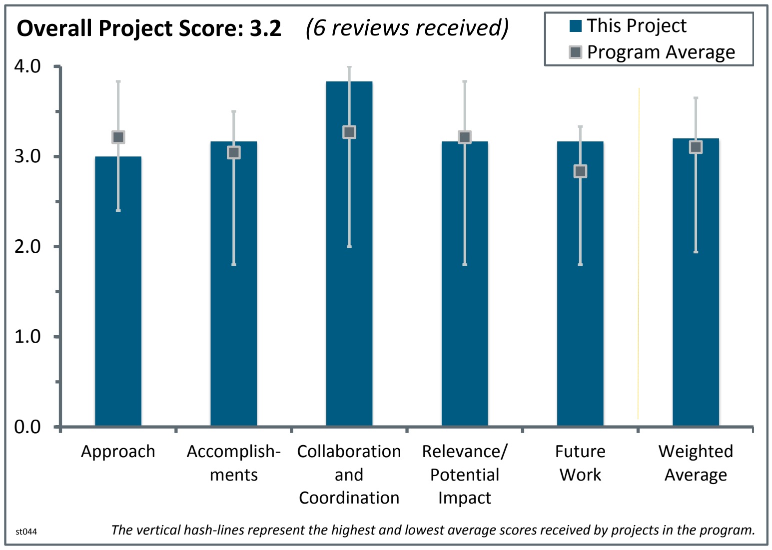
- The team should focus on $B_{20}H_{16}$ synthesis and characterization. This project should not be continued past the current budget period.
- Because this project is scheduled to finish by the end of fiscal year 2013, there are only a couple of suggestions regarding its future scope. It would be valuable if $B_{20}H_{16}$ could be successfully synthesized and if characterizations of its hydrogen desorption behavior along with NMR studies of the product phases could be completed within the scope of the project and reported to the hydrogen/fuel cell communities.
- The community seems to be in some agreement on the stability of the $B_{12}H_{12}$ anion and its role not as an intermediate but as a terminal borohydride sink in complex metal hydride systems. Perhaps the researchers should conduct modeling work on this to discover if there exist potential pathways out of this thermodynamic well or develop suggestions as to how to avoid this sink. This would seem to be a valuable contribution this team could make. Perhaps a challenge to this team is to come up with new methods to measure species diffusion rates through the materials that do not require national user facilities to accomplish the work. This might not be achievable, but it is worth brainstorming.

Project # ST-044: SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence: Design and Testing of Adsorbent Storage Systems

David Tamburello; Savannah River National Laboratory

Brief Summary of Project:

The objectives of this project are to: (1) develop and apply an adsorbent acceptability envelope, (2) conduct component adsorbent experiments, (3) design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, (4) validate model predictions, and (5) improve both component design and predictive capability. Savannah River National Laboratory (SRNL), in cooperation with its research partners, is evaluating solid-state hydrogen storage systems for vehicle application. Storage device design has been investigated through modeling and experimental development.



Question 1: Approach to performing the work

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

- Understanding how heat and gas flow through beds/pellets of storage material is and should be the key driver behind the entire Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center)—it was the whole reason for advocating for the creation of the Center. Knowledge gained from this project will undoubtedly lead to improved material level targets and alignment with research needs/resources.
- For the review period, the "Specific, Measurable, Achievable, Relevant, and Timely" (SMART) milestones include analyses to demonstrate sorbent and system capabilities exceeding the HSECoE system targets of 4.1 wt.% and 20 g/L. These targets are lower than the 4.1–4.4 wt.% and 24–25 g/L gravimetric and volumetric capacities of commercially available 700-bar compressed hydrogen systems.
- The approach used by SRNL involved heat simulations.
- This approach is generally effective but could be improved; it contributes to overcoming some barriers. It is unclear what the difference is between a SMART milestone and a Transport Phenomena Technology milestone. It seems the former all involve reports of some type, but it is unclear how more reports are going to solve the key problems of volumetric density and loss of useable hydrogen. This seems like an easy way to meet all of the milestones without having any skin in the game. Milestones should be quantifiable and relevant. A "report on the ability to develop and demonstrate a 3 minute refueling …" is essentially useless. Milestones are needed that state "Demonstrate a 3 minute refueling…."
- A well-developed and sensible approach has been adopted for modeling, designing, and testing engineering prototypes for adsorbent systems. The approach that was employed to rapidly down-select four system options from a huge number of possible system combinations is especially impressive. It would have been helpful to include an explicit statement of outstanding obstacles and challenges that must be addressed in the remainder of the project. Without that information, it is difficult to fully assess whether the approach focuses clearly on the critical remaining problems.
- The adsorbent acceptability envelope, combined with other models, clearly defines the properties needed for successful materials and systems. The Center's approach of using "idealized" materials to guide materials discovery clearly shows the difficulties in materials design and synthesis. There is no apparent

analysis of the impact of the technologies on forecourt configuration and costs. This is likely to lead to suboptimal solutions.

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

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

- The team has made tremendous progress in the last year. It feels like the effort and coordination of the previous years is bearing results and providing direction to the team. The team is beginning to learn the important trade-offs in heat and gas flow management associated with different material packing configurations.
- This project has achieved a significant improvement in cost (HexCell).
- Defining required properties for sorbents is a good development.
- Excellent progress has been made in 2012–2013 on developing an “acceptability envelope” for integrating material properties and system design. This will be critical for formulating an optimized solution for an adsorbent storage system. Good progress has also been made on developing solutions for effective flow-through cooling and heat exchange. Likewise, a comprehensive parametric analysis of a huge array of possible system options resulted in the identification of four adsorbent system designs optimized for heat transport and efficient hydrogen delivery. It would have been helpful to include some specific details concerning the sensitivity of overall system performance on variations in bed uniformity.
- Four systems have been evaluated; the updated spider charts show expected improvement in cost but little other improvement (for HexCell and modular adsorption tank insert [MATI]). The team has made significant progress toward meeting some of the barriers; however, a few key barriers remain (loss of useable hydrogen, and volumetric and gravimetric capacity). The team has also achieved accomplishments on idealized materials, including predicting an idealized material based on metal-organic framework-5 (MOF-5) using the desired system properties. Flow-through cooling with liquid nitrogen shows clear benefits, and tests at the Jet Propulsion Laboratory confirm improvement with liquid nitrogen, although not as much as predicted. It is unclear what the cost penalties are associated with liquid nitrogen cooling and how this impacts infrastructure at the forecourt.
- The SRNL/University of Quebec Trois Rivieres (UQTR) team has developed adsorbent acceptability envelopes for MOF-5-like materials assuming an 80 K storage temperature. For the next round of material discovery, attention must be paid to meeting the targets for not only system weight and volume but also energy efficiency (80 K is likely not acceptable) and cost. The decision to go with an all-metal, Type-1 aluminum tank should be revisited. Slide 17 shows that the metal tank in the four design options weighs between 80 and 110 kg and accounts for 53%–59% of the system weight. It is unclear how this design can lead to a go decision for Phase III. It is also unclear if this thermal mass can be cooled from 180 to 80 K in 3 minutes and what the penalty is in system efficiency due to this amount of cryogenic cooling.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration is very convincing.
- This project is clearly well coordinated with activities at other institutions in the Center.
- The principal investigator (PI) is part of the HSECoE—this is the best collaboration in the U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program. Other DOE programs should emulate this model.
- The presentation lists close-knit collaborations with other members of the HSECoE. No interactions were mentioned with people and organizations outside of the Center.
- The Center has assembled a strong team with good collaboration between original equipment manufacturers, national laboratories, and the Center. It is unclear whether material target properties are being communicated to material developers.
- A hallmark of the HSECoE is the positive impact that inter- and intra-organization collaborations have made on the overall success of the Center’s activities. This project is no exception. Fruitful and technically

important collaborations have been established with multiple partners in the Center and with external organizations. These collaborations have served to significantly leverage the SRNL activity.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This project fits perfectly into the Hydrogen and Fuel Cells Program (the Program). It is relevant and necessary.
- This project is a critical component of the overall HSECoE effort. The project incorporates innovative design concepts and system integration approaches for a storage system based on high-surface-area adsorbents. It addresses the principal DOE goals and targets and is directly relevant to DOE RD&D objectives.
- There is excellent trade-off analysis between the MATI and Hexcel designs—these systems will likely have different applications for different materials. The project team should keep refining work on both systems and highlight the advantages and disadvantages of each.
- For Phase II, this project is developing an adsorbent acceptability envelope, conducting adsorbent experiments, and designing components and test fixtures.
- Because none of the materials being studied by the Center appear to be viable, its relevance is certainly limited. Knowledge gained may or may not be applicable to viable materials.
- The project is focused on the Program's goals and objectives delineated in the *Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan*, but it is not clear how much advancement will be made. The loss of usable hydrogen and volumetric capacity remain far from targets and should be addressed. The value of systems engineering seems to have run its course and it is clear the remaining barriers cannot be addressed by optimizing the system. Engineering efforts should be coordinated with materials research efforts and should be limited to small prototypes until new materials are identified that may meet the volumetric/gravimetric and hydrogen loss targets.

Question 5: Proposed future work

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

- The project team should carry on with its work.
- The proposed future work should be done as planned.
- The future work builds directly on the current efforts, especially in the areas of thermal transport/cooling and experimental validation of system models. Unlike the situation with a more complex chemical hydrogen system, the integration, scale-up, and testing of a practical system based on a cryo-adsorption medium seems far more straightforward. The pathway and plans for prototype development in Phase III follow directly from the Phase II effort and seem appropriate and reasonable.
- The future work may need clearer definition; for example, "additional model development (as required)" needs to be more specific.
- The PI clearly laid out the future work in support of the Phase III prototype design. Because of the complex interactions and relationships with other teams, it is difficult to judge the contributions of the SRNL/UQTR team.
- Plans may lead to improvements, but they need to be better focused on overcoming barriers. Future work includes "Increase Material Capacity to 140% and ultimately 200% of Powdered MOF-5"—it is not at all clear how this will be accomplished.

Project strengths:

- This project has strong collaboration with UQTR and other members of the Center.
- The project has made good progress toward reducing system cost for both Hexcel and MATI.
- This project features a strong industry/laboratory/university team.

- The project is being conducted by a well-qualified team with background and expertise in all areas relevant to the development of a successful prototype system for a cryo-adsorbent storage system. The technical approach is solid and plans for future work build directly on the excellent progress that has been made in the Phase II effort. The technical effort by the SRNL team is augmented by useful collaborations with Center partners and external organizations.

Project weaknesses:

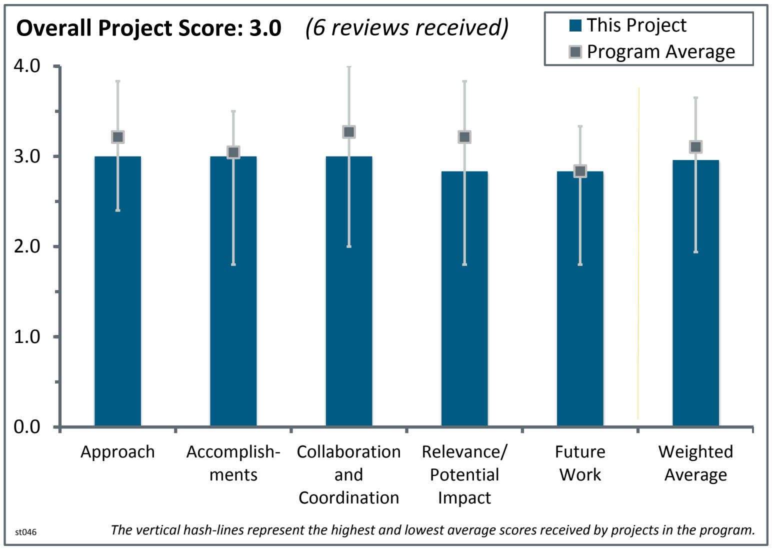
- It is not clear if the best decisions have been made about flow-through cooling, 80 K storage temperature, Type-I tanks, interim weight and volume targets, etc. The net result is that the adsorption system does not look very viable.
- The project is far from meeting key barriers to the loss of usable hydrogen, volumetric density, and gravimetric density. It is unclear from the future work how these barriers will be addressed.
- There is no consideration of forecourt costs and implications. Optimization of an onboard system without considering the impacts on hydrogen costs and overall greenhouse gas issues may result in sub-optimal solutions.
- It is highly unlikely that a system based on MOF-5 will meet the DOE targets for hydrogen storage. However, the development of a prototype system based on the best available surrogate material(s) (e.g., MOF-5) will hopefully provide information that will translate directly to an optimized system based on a storage medium with improved properties.

Recommendations for additions/deletions to project scope:

- Validation of the models is planned and is required. System scale-up and future system predictions are planned and are also are required.
- It may be too late to add or subtract tasks. DOE needs to make sure that the data and methods are properly documented and available to organizations outside of the HSECoE.
- System optimization is unlikely to change issues associated with hydrogen loss and volumetric/gravimetric densities. Only MOF-5 is currently being considered—this is understandable because the project is focused on engineering a system—however, more materials research is needed to address key barriers.
- A more explicit and detailed statement of the remaining risks and challenges should be provided. Without that information, it is difficult to assess whether the technical effort is focused on the critical problems that really need to be solved.

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

Kevin Drost; Oregon State University



Brief Summary of Project:

The objectives of this project are to use the enhanced heat and mass transfer available from arrayed microchannel processing technology to: (1) reduce the size and weight of storage, (2) improve the charging and discharging rate of storage, and (3) reduce the size and weight and increase the performance of thermal balance of plant (BOP) components. Arrayed microchannel processing technology has the potential to reduce storage system size and weight; offer a high degree of control over the process; maintain the optimum performance attained in a single cell; add complexity without increasing cost; allow rapid start-up and response to transients; and provide attractive high-volume, low-cost manufacturing options.

Question 1: Approach to performing the work

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

- The Oregon State University (OSU) project addresses system volume and weight, hydrogen charging/discharging, and BOP. The work is tightly focused on microchannel-based concepts for managing hydrogen storage and thermal energy balancing. Modeling and bench-scale research are effectively carried out to provide a sound basis for evaluating the engineering and economic tenability of a microreactor-based approach to onboard hydrogen storage. The overall approach still needs engineering-scale vetting before a convincing argument can be made for raising this concept to the top of the list of candidates.
- The microchannel processing technology approach that has been adopted in this project is unique and innovative. It specifically addresses systems in which diffusion-limited processes inhibit thermal transport. The approach provides a potentially novel and elegant solution to improving charging/discharging rates and reducing the weight and cost of critical BOP components required for the prototype storage subsystem. The approach comprises a good combination of modeling/simulation and experimental validation. The use of microchannel assemblies for thermal transport together with modular adsorption tank inserts (MATI) is especially interesting because it can be used to enhance media conductivity and to facilitate use of a wider range of cooling options.
- OSU is a partner in the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center). The primary objective of the HSECoE is to address critical engineering issues that impede the development of materials-based hydrogen storage systems from meeting the U.S. Department of Energy (DOE) targets for fuel-cell-powered passenger vehicles. The role of OSU is to employ microchannel technology (MT) that enhances heat and mass transfer within components to reduce the weight, volume, and cost of the storage systems. This project does not directly influence the selection of composition of the storage materials themselves. The present focus is on adsorption hydrogen storage.
- The project's approach features MATI. Both experimental validation of model pellets and compaction have been completed.
- The project uses both simulation and experimental investigations to identify, prioritize, and evaluate the best novel microchannel designs for onboard applications. Test results are then used to validate the predictive tools.

- The project would be improved by having a well-defined baseline for conventional heat exchanger technology.

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

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

- Good progress was made on this project in 2012–2013, especially in the fabrication and testing of the single- and multi-module MATI assemblies and the initial work on thermal conductivity enhancement in densified metal-organic framework-5 (MOF-5) cryo-adsorbents. The "needle insert tests" provide a useful methodology for improving thermal conduction in densified MOF-5 ("hockey puck") samples. However, the final engineering embodiment of this approach is unclear. The design and testing of the 1 kW microchannel combustor for hydrogen heating during cold-start simulations and experimental results validated the concept and provided a straightforward pathway to further development and improvement of the thermal transport subsystem in the next phase of the project.
- The OSU presentation reported modeling and experimental results in a host of areas related to the microchannel reactor concept. Most of the critical issues are being addressed in a clearly thought-out and well-orchestrated manner for both the MATI and the microchannel combustor/recuperator. Qualification of aluminum as a suitable material for microlamination led to a significant cost reduction. Good agreement was achieved between modeling results and experimental measurements during Phase II adsorption bed tests.
- Work is in progress to revise the MATI design to accommodate a multi-modular stack for adsorption bed testing. Simulation of hydrogen charge/discharge cycles indicates that additional heat conduction is needed to meet the DOE target for hydrogen refueling rate. The principal investigator (PI) has proposed inserting solid pins in the MOF-5 bed to promote conduction enhancement. The project has tested a 1 kW microchannel combustor/heat exchanger for hydrogen heating during cold starts. Results meet the "Specific, Measurable, Achievable, Relevant, and Timely" (SMART) goals for 85% efficiency, 0.9 kg in mass, and 0.6 L in volume. Aluminum-6061 has been qualified for use as a construction material for both the MATI and the combustor/heat exchanger.
- During their Phase II efforts within the HSECoE, OSU researchers have been working on two applications for their MT capabilities: (1) MATI and (2) microchannel combustor-recuperator for hydrogen conditioning (MCRHC). The MATI could facilitate heat transfers within the tank using compacted adsorbents while the MCRHC could burn portions of hydrogen released at temperatures circa 200 K or lower to supply the fuel cell power system with hydrogen gas heated above minimal operating temperatures. OSU has designed, analyzed, and built simplified prototype configurations of the MATI and MCRHC. Feasibility testing of a simple prototype of the MATI has started. Cost projections for mass manufacturing of these devices were made, although there is still a need for refinements in designs and manufacturing. Specific configurations for Phase III development and testing have not yet been completed.
- The amount of work done does not seem to justify the $2 million DOE spent on this project when compared with other projects with similar funding. Although the system can deliver 0.41 g/s, it is not obvious that this meets the target requirement (0.02 g/s/kW). This would supply a 20 kW fuel cell, but that is much smaller than a typical automotive fuel cell.

Question 3: Collaboration and coordination with other institutions

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

- OSU is a member of the HSECoE and it has strong collaborations with other members of the Center.
- OSU has interacted with several of the HSECoE partners to determine what roles are best suited for the MT. These interactions led to design refinements of the MATI and MCRHC components. With input from Pacific Northwest National Laboratory and others, OSU has provided predicted manufacturing costs and configurations for adsorption storage systems.
- Strong collaborations with other technologists in the Transport Phenomena and Enabling Technologies groups in the HSECoE are reinforcing and augmenting the work in the OSU project. Several collaborators

are providing useful input to the MATI heat exchanger and enhanced puck conductivity efforts. The microchannel combustor work is being conducted in close cooperation with Savannah River National Laboratory and the Jet Propulsion Laboratory. These collaborations are ensuring that the OSU work remains closely connected to the overall HSECoE mission and provides important industrial and government laboratory perspectives to the university-led activity. Closer collaboration with the General Motors thermal management activity is recommended.

- Collaboration and coordination of research and development (R&D) activities at OSU with other HSECoE partners is reported to be appropriate and well established. Slide 30 contains a reasonably detailed summary of OSU's connections with several of the other Center partners, but this connectivity is not obvious in the results slides. It seems that OSU plans and conducts its own research, then reports to the other partners. It would be useful to clarify how the collaborations listed on slide 30 actually work. This is important because the devices being developed by OSU need to fit seamlessly into the overall system architecture evolving within the HSECoE.
- Strong interaction with some HSECoE system groups has been discussed. An even stronger interaction with the Adsorbent System group is suggested as optimization of compaction and system should go hand in hand.
- Collaboration is limited to the HSECoE.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.8** for its relevance/potential impact.

- This project is focused on applying MT for heat and mass transfer enhancement to reduce onboard system weight and volume and to improve hydrogen charge and discharge rates.
- The MATI and MCRHC can potentially reduce the mass and volume of adsorption storage systems while enhancing thermal performance. The unresolved issues include the added costs of these components and their durability during extended operation. The issues of fabrication of the internal structures using aluminum materials and the assembly of the MATI within light-weighted storage vessels have been incompletely addressed.
- The OSU message regarding relevance is that microchannel approaches can solve most (if not all) of the nagging barriers confronting onboard hydrogen storage, hydrogen delivery (to the fuel cell), recharging, and thermal energy management for fuel-cell-powered vehicles. OSU's modeling results support this message. What is currently needed is an appropriately scaled demonstration with a convincing outcome.
- This project employs microchannel processing technology to enhance thermal transport rates in specially configured (MATI) cryo-adsorbent media assemblies and to increase the performance of thermal BOP components for improved cold-start applications. This project addresses two important problems in cryo-adsorbent prototype storage system development. It supports the mission of the HSECoE and it is directly relevant to the DOE RD&D objectives.
- Without baselines for conventional heat exchanger designs, it is impossible to rate the relevance of this project.

Question 5: Proposed future work

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

- OSU's plans for the coming year seem to be right on target. These plans are not extensive, but they are the next logical steps to take toward a definitive demonstration of the microchannel approach. Issues with respect to refueling time and heat transfer in the bed remain to be resolved.
- The proposed future work is a continuation of the work in progress and an improvement of the MOF-5 hockey puck to meet the hydrogen charging rate.
- The proposed future work is a direct extension of the current effort. The future plans for assembly and testing of the multi-cell microchannel/MATI assembly are straightforward. However, the plans are unclear for enhancing the conductivity in a MOF-5 puck beyond the levels measured in the current work. It would have been helpful if more detail had been provided. Likewise, remaining obstacles, challenges, and

potential problems have not been presented. It is difficult to adequately review the future plans without knowledge of the specific problems that must be addressed.

- During Phase III, fabrication issues and laboratory testing of the prototypes for both devices should be the researchers' major emphasis in order to verify their simulations of thermal performance. They also need to address issues and problems during component building and operating conditions. Based on the extent of testing performed at OSU during the past four years, it is not clear that sufficient assessments of thermal performance will be completed on new prototype devices during the duration of the project. For example, OSU has not yet built or tested devices that scale from a single unit of a compacted adsorbent to more highly integrated versions during Phase II.

Project strengths:

- This project team features sound knowledge and capability in microchannel devices.
- The PI has a long history of research in MT. The project is well focused on meeting the technical objectives and targets defined by DOE and the HSECoE.
- The OSU project is directed by a bona fide expert in the field of microchannel device development. The research addresses a wide range of issues cleverly and effectively.
- OSU has experience with developing and fabricating MT devices for various purposes that suggest these assemblies can be suitable for those hydrogen storage components requiring improved heat and mass transport.
- This is an innovative project that is being conducted by a well-qualified R&D team. Good collaborations with other HSECoE groups are ensuring that the project remains focused on important goals for subsystem development.

Project weaknesses:

- There is a lack of a clear baseline for comparison with other technologies.
- The current MATI design will not meet the target charging rate because of limited thermal conduction.
- Stronger interaction with the materials groups would be desirable. Optimization of the MT should go hand-in-hand with materials optimization.
- There is much that still needs to be verified in regard to the microchannel-based approaches under study at OSU. These include the robustness of the beds, gas distribution within the beds, and the final story on manufacturability at an acceptable price. Also, it is hard to accept the notion that flow path plugging will not be a problem at some level.
- A detailed statement is needed concerning specific technical obstacles, challenges, and risks. More detailed plans for enhancement of MOF-5 thermal conductivity that are consistent with a prototype engineering system should be provided.
- It is not apparent whether the as-conceived MATI and MCRHC 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 could lead to very serious problems. It is one thing for models to predict high-performance behavior under idealized scenarios in contrast to fabrication and assembly of the suitable components for testing.

Recommendations for additions/deletions to project scope:

- The proposed future work seems to be the best path forward for OSU. The experimental system tests planned for the coming year need to demonstrate sustainable/robust microchannel device performance.
- OSU should continue to verify its conceptual designs for the MATI and MCRHC devices via experiments. In particular, demonstrations should show complete and reliable separations (i.e., no internal or external leaks of heat exchange fluids) during operation. Because heat transfer and gas permeation with their compacted carbon samples appear to be issues, proposed improvements should be evaluated via laboratory testing.
- Permeability and thermal conductivity are key issues in the optimization of such a design. The influence of compression on the achievable permeability and storage densities could be easily measured by having

collaboration in the area of in situ neutron imaging. For example, using a single compact that was compacted inhomogeneously, materials properties could be optimized easily.

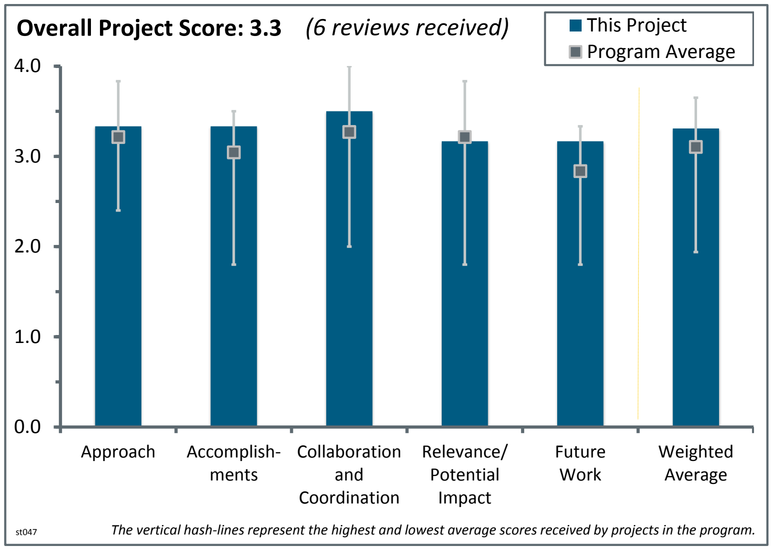
- Because it is unlikely that MOF-5 will meet the overall DOE storage targets, it will be important to understand the extent to which the concepts and test assemblies developed here can be extended to other (hopefully improved) cryo-adsorption media.

Project # ST-047: Development of Improved Composite Pressure Vessels for Hydrogen Storage

Norman Newhouse; Hexagon Lincoln

Brief Summary of Project:

The objectives of this project are to: (1) identify appropriate materials and design approaches for the composite container; (2) maintain durability, operability, and safety characteristics; and (3) develop high-pressure tanks for hydrogen storage. The project will also identify pressure vessel characteristics and opportunities for performance improvement. High-pressure tanks should contain appropriate materials and operate safely and effectively at defined pressures and temperatures.



Question 1: Approach to performing the work

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

- Barriers are directly addressed in this project.
- The project employs a systematic approach to addressing the design and cost aspects of storage development.
- The approach is well thought out and consistent with the objectives of the Hydrogen Storage Engineering Center of Excellence (HSECoE, the Center). The switch from Type 4 to Type 1 tanks reflects the revised pathway for Phase 3 being adopted by the HSECoE.
- Hexagon Lincoln (HL) is sharply focused on crucial aspects of onboard hydrogen storage issues. The barriers addressed and the stipulated targets with respect to system weight, volume, and cost are the areas where gaps are the largest and most uncertain. Clearly, pressurized gas is at the top of the hydrogen storage method-of-choice list for good reasons. It is less complex (e.g., fewer components), less costly, and has less built-in uncertainty than the storage-materials-based approaches. The level of feasibility appears to be very high. HL is at center stage in the tank development part of the HSECoE.
- HL is a partner in the HSECoE. The primary objective of the HSECoE is to address critical engineering issues that impede the development of materials-based hydrogen storage systems from meeting the U.S. Department of Energy (DOE) targets for fuel-cell-powered passenger vehicles. The identified role of HL 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 selection of the composition of the storage materials themselves. The focus of HL during Phase II was on the cryogenic properties of composite tanks being considered for adsorption hydrogen storage.
- It should be clearly mentioned that this project is dealing with pressure vessels for cryo-absorbent systems only. Test procedures should be described. For a better understanding, the correlation between a specific barrier, the approach, and the result should be described.

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

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

- There has been good progress with the tests and the approved design approaches.

- Vessels have been designed, manufactured, and successfully tested. Selected vessel types will be available to other HSECoE partners for subsidiary component testing during Phase 3. Performance improvements in regards to weight, available volume, and cost have been realized through HL's achievements. Problems with the liner and boss junctions persist, but HL has plans to address these matters.
- Cryo-testing of subscale Type 4 tanks showed that the liner leaked at >3,300 psi. Cracks initiated at the boss/liner interface where stress level was high and there was a mismatch in the coefficient of thermal expansion between boss and liner materials. The Type 1 subscale tank was fabricated and tested at ambient temperature and at 80 K. The tank was cycled 200 times to service pressure at 80 K. It is necessary to cycle the tank to 5,500 cycles to be in compliance with SAE J2579. Hydrostatic pressure burst tests should be conducted at 3.5 times service pressure for Type 1 welded containers (FMVSS 304). There was no data presented on carbon fiber (CF) composite properties for the Type 4 tanks. It would be very useful to DOE if HL reports its findings on the translation efficiency, composite tensile strength, and modulus.
- For the development of adsorption hydrogen storage tanks, HL evaluated the cryogenic behavior of both Type 4 cylinders (i.e., CF wrapped with polymeric liners) and Type 1 (aluminum metal). The impact of extreme operating temperatures on these cylinders at cryogenic conditions was demonstrated from low-temperature leak, cycling, and burst tests. HL showed that no current polymeric liner material is suitable for Type 4 tanks that are to be operated at cryogenic conditions, although aluminum-based Type I tanks are adequate and sufficiently robust when pressures do not exceed about 100 bar. So far, there has been minimal consideration by HL of how the interior of these cylinders are loaded with sorbent material and enhanced heat transfer internal structures.
- Challenges arose with Type 4 designs at very low temperatures and it is not yet clear if these can be overcome for some applications. The Type 1 design shows promise with simpler media loading aspects. The weight penalty associated with the Type 1 design could be acceptable for some systems.

Question 3: Collaboration and coordination with other institutions

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

- The partners represent a broad pool of top talent.
- It seems that all relevant partners for cooperation are involved.
- HL maintains good collaboration and interaction with HSECoE partners.
- The project has adapted to the changing parameters arising from the work of the well-coordinated collaborators.
- HL interacted with several HSECoE partners on the cryogenic properties of Type 1 and Type 4 vessels during Phase 2. A separable Type 1 aluminum metal vessel was developed to permit Phase 3 tests on a metal-organic-framework-5 (MOF-5)-based adsorption prototype, which can include internal structures for thermal management.
- HL's tank work is important to the entire HSECoE. Collaboration within the HSECoE on tank issues seems to be close and effective, as indicated on slide 17. A patent application with Pacific Northwest National Laboratory is in progress for the external vacuum insulating vessel concept. Vessel criteria are reached by consensus within the HSECoE.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Cryo-storage will deliver a significant improvement in capacity.
- The project is addressing an important element for several developing onboard hydrogen storage technologies.
- Pressure vessel development is at the top of the relevancy list for the HSECoE. Everything HL is doing and will do in Phase 3 is as relevant as it gets because it looks like pressurized hydrogen gas will be the top choice for full system validation.
- This project is dealing with the vessel for an adsorbent system. The first step is to develop the adsorbent material itself, so this project is assessed only as "good."

- Characterization of the limitations of using Type 4 vessels for hydrogen storage at elevated pressures and cryogenic temperature is important information to share with the fuel cell community. While HL has not identified a solution to the issues of using polymeric liners in cryogenic vessels, it has shown the need for discovery of materials to meet these conditions.
- HL develops both Type 1 and Type 4 vessels in support of sorbent storage options selected by the HSECoE. The work on Type 4 vessels is relevant to meeting DOE's 2017 targets for system weight and volume. However, systems using Type 1 vessels will have no chance of meeting the DOE weight target.

Question 5: Proposed future work

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

- The proposed work is straightforward.
- The project has identified multiple paths forward as contingencies for storage development.
- Three types of tanks are at various stages of design/manufacturing/testing. The Type 1 tank already looks pretty interesting. Things can only get better. Specific performance improvement needs have been identified and will continue to be addressed in Phase 3.
- The future plans shown on slide 18 would be useful for the Phase 3 activities of the HSECoE partners involved with adsorption storage. Namely, continuing work would be on identifying and characterizing materials for operation at cryogenic temperatures along with assessing the consequences of cycling. Development of designs that facilitate the filling and sealing cylinders with sorbent materials is also important. The large mass of the sealing region for the Type 1 Phase 3 tank is an issue that should be examined closely to see if other configurations with reduced mass can be designed.
- The characterization of fatigue in Type 1 tanks needs to be addressed as part of pressure cycling at cryogenic temperatures. Switching to Type 1 tanks has increased the system weight significantly, making it practically impossible to meet the DOE gravimetric capacity target. Further development of Type 4 tanks at 80 K should only be continued after successful qualification of the materials (e.g., tensile impacts) at service temperatures.
- There are a lot of tasks planned for future work. There are tests planned with different vessel types (Type 1, Type 3 and Type 4). It is difficult to understand the strategic approach behind these tasks.

Project strengths:

- The testing involves actual hardware.
- A vessel manufacturer that has a lot of experience with regard to vessel behavior is doing this project.
- HL has substantial experience in developing and manufacturing high-pressure tanks for onboard hydrogen storage.
- The project brings deep experience in storage design to the development of tanks for challenging operational characteristics.
- HL is a commercial vendor of high-pressure gas cylinders for a range of applications. This background has been helpful during the HSECoE assessments of costing and manufacturing issues for hydrogen storage vessels along with clarifying safety requirements and procedures.
- The project's strengths include a knowledgeable principal investigator, very good connectivity and consensus building within the HSECoE regarding tank issues, and a high probability that further performance improvements will be forthcoming during Phase 3.

Project weaknesses:

- Hopefully HL has enough resources left to take tank performance parameters to yet another level during Phase 3.
- The requirements for the tests are not clear (e.g., references to SAE, ISO, etc.). The test descriptions should be attached in the backup.
- HL does not appear to consider possible contaminations issues due to outgassing or decomposition of the storage materials, or how tanks need to be constructed and loaded with these sorbents. There seems to have been very limited publication on the work performed during Phases 1 and 2 of this project. Dissemination

of the cryogenic properties and limitations of Type 4 vessels would be valuable to the entire hydrogen energy community.

Recommendations for additions/deletions to project scope:

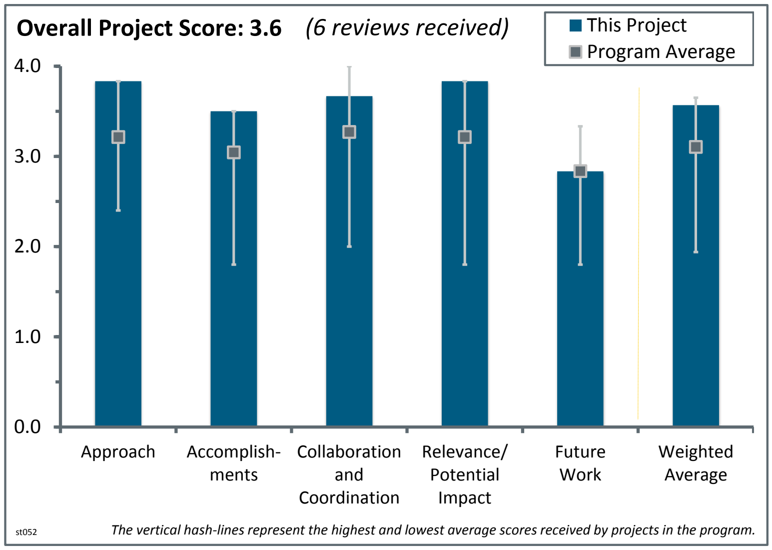
- The cryo-scope and comparison to alternatives could be better described at the start to give the reviewers a better sense of this technology.
- For the coming year, testing with hydrogen (instead of nitrogen) seems important. There may be embrittlement issues that are getting missed by using a surrogate for hydrogen. There is likely an extra “7” in the “Project Funding” total on the second slide; if not, the tanks must be more expensive than realized.
- HL should aggressively address design issues for assembling, filling, and sealing sorbent-containing vessels. This includes looking at chemical compatibility as well as conducting extensive pressure and temperature cycling. In addition, more effort should be made to find and characterize polymers that would reliably serve as liners in Type 4 tanks operating at cryogenic temperatures over the pressure range of 1–350 bar.
- The researchers should consider pressure cycling tests for up to 5,500 cycles to meet SAE guidelines. They need to quantify the fatigue characteristics of Type 1 tanks (a plot or at least a few data points of burst pressure versus number of cycles would be nice). Further development of Type 4 tanks at 80 K should only be continued after successful qualification of the materials (e.g., tensile impacts) at the service temperatures. Investigation of Type 3 tanks is recommended as a compromise between weight and cost. The team should report data on the translation efficiency, composite tensile strength, and modulus for Type 4 tanks.

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

Karl Gross; H2 Technology Consulting LLC

Brief Summary of Project:

The objective of this project is to prepare a reference document detailing best practices and limitations in measuring the hydrogen storage properties of materials. The reference document will be a guide to reduce errors and improve efficiency in measurements, improve reporting and publication of results, reduce the need for extensive validation, and allow experience and knowledge to grow and expand in the field of hydrogen storage. This project's goal is the establishment of uniform practices in the measurement and presentation of hydrogen storage materials performance.



Question 1: Approach to performing the work

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

- The reference document covers various aspects of hydrogen storage materials. The tasks and chapters have been broken down into very logical and easy-to-follow practical subject areas.
- The basic idea to prepare a reference document detailing best practices for a variety of relevant measurements, their limitations, and error propagation is extremely useful to the hydrogen storage research community. It is really good that this document is publicly available.
- This magnum opus represents a labor of love for Karl Gross, but it also serves as the definitive manual on best practices for scientists and engineers working in the area of hydrogen storage. Dr. Gross is a first-rate experimentalist and he has distilled and collected material from a wide range of external sources in addition to collating wisdom and know-how developed within the U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program over the past decade. The document is still a work in progress, but it already defines the state of the art and will do so for many years to come.
- The principal investigator (PI) has assembled a group of internationally recognized experts to assist in the writing and review of this document. The authors have described the techniques and best practices for measuring and characterizing the hydrogen storage properties of new and existing materials in a complete and comprehensive way. A careful and very thorough approach was used to prepare the document. It is well organized and includes both introductory material and more detailed information about each topic. A comprehensive resource document that discusses uniform practices and issues in the measurement of hydrogen storage material properties will be of great benefit to the research, development, and engineering communities. In many ways, it is unfortunate that this resource was not available 5–10 years ago.
- The major objective of this project is to identify the appropriate methodologies for obtaining reliable measured data on the critical physical and chemical properties of hydrogen storage materials. The approach is to describe the advantages and limitations of common methods being used to characterize the hydrogen capacity, reaction kinetics, thermal properties, and other engineering parameters necessary to develop materials with the potential to meet the corresponding DOE performance parameters. An especially important aspect is to avoid classifying poorly conceived or conducted experiments as the discovery of "outstanding" hydrogen storage candidates; this wastes resources and diverts attention from more realistic materials. Unfortunately, many researchers choose not to heed this information. The emphasis during the past year has been on engineering properties, including thermal management issues.

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

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

- Over the past several years a comprehensive and reliable online treatise has been produced. The recent topics contain the same high-quality descriptions and illustrations of principles.
- A very useful document has already been created and the final part, focusing on thermal and mechanical properties, is in good progress.
- Both engineering thermal and mechanical properties are very important for practical application of the hydrogen storage materials.
- While it is true that several sections remain to be completed, the magnitude of the task and the importance of the final product indicate that progress this year has been excellent. Several key sections have been completed and the final few are well underway.
- This document is the culmination of a multiyear effort. Although some additional work on selected sections remains, the document is essentially complete. The project represents a tremendous amount of work by a large number of highly skilled experts in the field. All of the major hydrogen storage material properties and characteristics (e.g., kinetics, capacity, and thermodynamic stability) and measurement methods are discussed in detail, and well-reasoned recommendations for best measurement practices are provided. Given the difficulties and confusion in making accurate physisorption pressure, concentration, temperature (PCT) measurements, the addition of a section (at DOE's request) that provides more in-depth analysis of the sources and propagation of errors in those measurements is useful and important.
- It is not uncommon for a project with so many stakeholders and reviewers to be somewhat cumbersome to make final versions, and it has been true in this case. This is particularly true for the error analysis section, which is one of the more crucial sections for this document to be an authority. It is not clear how much work beyond literature surveys and previous work has actually gone into engineering and mechanical properties—the subject of much of this year's work.

Question 3: Collaboration and coordination with other institutions

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

- This is a document by consensus. Many of the experts in the relevant areas have been included in its drafting. The collaboration and coordination are exceptional.
- This project has a large group of collaborators from various fields in hydrogen storage materials; each brings in different expertise and makes this project a well-coordinated effort.
- Dr. Gross has recruited recognized experts to assist with and contribute to the project, such that each section represents the consensus of several leaders in the field.
- Numerous world experts in the field have contributed to the writing and review of this document. The PI has done a first-rate job of soliciting their input on specific sections and utilizing their considerable talents to create a comprehensive, well-organized, and eminently readable document. In addition, an important chapter on best practices for physisorption PCT measurements is being prepared in (an official) collaboration with the National Renewable Energy Laboratory (NREL).
- While a larger number of contributors were involved in the preparation of most of the earlier chapters, it appears that much of the last two chapters was based on the literature as well as some contribution from a staff member at Savannah River National Laboratory.
- Currently, there is much focus on low-weight element borohydrides for hydrogen storage. A huge number of recently published scientific literature describes the structure and reactions with other hydrides. But there is limited knowledge about the decomposition reactions and virtually no information about the mechanism for re-hydrogenation. This highlights that the project presented by Dr. Gross is highly relevant. There is a significant lack of general knowledge and understanding of the exact thermodynamic, kinetic, and "system" data. This project provides the fundament for performing systematic investigations, potentially worldwide.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This work will define best practices in hydrogen storage for years to come.
- The goals and aims of this project are extremely important. The only potential issue in creating a best practices guide is having the myriad of researchers actually use it.
- This document provides the community with some common measurement tools that can reduce the measurement error, improve the efficiency, and reduce the cost of extensive validation.
- It is very important to include engineering aspects such as thermal and mechanical properties as planned. Hopefully, it can be accomplished within the limited time this project has left.
- All of the thermal properties and engineering parameters being included in this project are relevant to the design, analyses, and operating behavior of hydrogen storage devices. Collecting this information within one document, albeit nearly 300 pages, should be beneficial to the purposes of the Fuel Cell Technologies Office's Hydrogen Storage program.
- Unlike other projects in the Hydrogen Storage program portfolio that focus on developing either materials or systems that meet the DOE targets for onboard hydrogen storage, this project is aimed at creating a comprehensive guide to metrics and best practices for measuring hydrogen properties of storage materials. Given the disparate and sometimes erroneous results that have been obtained by the hydrogen storage community (even on the same samples), there is a great need for a resource document that can be used to ensure that measurements are being made correctly and are in line with best practices. The best practices document prepared by the PI and his collaborators is well written and comprehensive and should provide both new and experienced workers in the field with a common basis for conducting measurements on the hydrogen storage properties of materials.

Question 5: Proposed future work

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

- The PI and all of the co-authors are very skilled scientists; furthermore, a long list of high-profile international collaborators are also involved. This proves that the project is extremely well organized and productive.
- The project is at a stage where the remaining tasks define themselves.
- Finalizing the document is a fair goal and needs to be done. The timescale for this is not outlined, nor is the amount of effort it will take.
- The engineering mechanical properties chapter seems to not include the pelletized hydrogen storage material property analysis.
- All of the topics relating to future tasks shown on slide 22 are worthwhile tasks to be included in the best practices document. However, neither the gas permeation nor the materials compatibility tasks warrant the in-depth treatment that was given to the thermal and mechanical engineering areas. However, brief overviews of key issues, some representative examples, and references probably would be sufficient at this time.
- The future work includes completion and review of the section on engineering mechanical properties and the integration of the results from NREL's work on sources and propagation of errors in PCT measurements on physisorption materials and on methodologies and best practices acquired from NREL's project on spillover characterization and evaluation. These will be useful and important additions to the already comprehensive resource document.

Project strengths:

- This project features excellent work from a universally respected practitioner. Key experts and specialists have been involved in and provided input for each section.
- The community involvement is outstanding and will help to create an authoritative document for best practices in the broad fields of hydrogen storage.

- This effort provides an independent assessment of the methodology being used to evaluate hydrogen storage materials. It has heavily involved outside contributors and reviewers to provide both depth and balance in various subject areas. Much of the first chapters are based on the personal research and professional experiences of the PI. The contents are extremely comprehensive and contain good illustrations of key concepts and limitations in the conduct of measurements.
- This project has a large number of collaborators from various fields in hydrogen storage materials; each brings in different expertise and makes this project a well-coordinated effort. This document provides the community with a valuable tool for hydrogen storage materials research.
- The PI and all of the co-authors are very skilled scientists; furthermore, a long list of high-profile international collaborators are also involved. This proves that the project is extremely well organized and productive. The document produced, so far, is very well written, informative, and useful.
- This multiyear effort is a "tour de force." No other single text can compare with the scope and breadth of the resource material that is given here. The author has assembled a team of world experts who have contributed to writing and reviewing the document. It will be extremely valuable for the research and development and engineering communities.

Project weaknesses:

- It is unfortunate that this resource was not available 5–10 years earlier.
- The timescales and project effort are not delineated; bottlenecks are not identified.
- In the engineering property chapter, there is a need to add more in-situ measurement techniques.
- The time taken from commencement to completion is significantly longer than initially anticipated. This may be seen as a drawback, but it comes at no extra cost and represents value in the final product.
- As the online best practices document has grown to more than 800 pages, it has become more difficult for the reader to digest all of the topics and contents. In other words, it has become challenging "to see the forest for the trees." Because several chapters were written 5 or 6 years ago, many of the cited references have become dated, while relevant—but more recent—publications and books are not mentioned. As examples, papers reporting round-robin testing involving several international laboratories on hydrogen-carbon and MgH_2 reference materials were published in 2009 and 2013, respectively. From examinations of these papers, it is clear that serious errors are being made because researchers are not following proper methods to produce reliable data. Although the "Best Practices" document has been available for years, it does not improve the quality of the reported data unless the actual researchers read and adapt the recommendations.

Recommendations for additions/deletions to project scope:

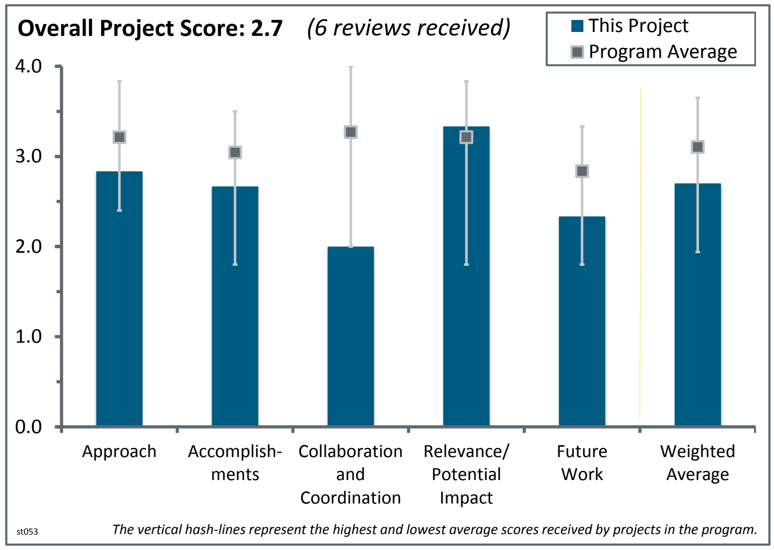
- This best practices project should be supported through the completion of Chapter 7, which is entitled "Engineering Mechanical Properties"; however, additional, new topics should not be added to its scope. Instead, the first chapters should be revised and updated with brief supplemental additions focusing on more recent research papers and books on hydrogen storage technology.
- The researchers should add the in-situ measurement tool to the engineering thermal properties chapter and add pellet mechanical properties to the engineering mechanical properties chapter.
- Complete and reliable measurements on engineering properties will be crucial for the next stage of hydrogen storage system development. The last chapters should also be completed and reviewed. Researchers should continue this project and include other experimental techniques as well, such as thermal analysis and spectroscopies.

Project # ST-053: Life Cycle Verification of Polymer Liners in Storage Tanks

Barton Smith; Oak Ridge National Laboratory

Brief Summary of Project:

The objectives of this project are to perform thermal cycle durability qualification measurements on polymeric tank liner specimens and assess the ability of liner materials to maintain the required hydrogen barrier performance. The project will devise and publicize test procedures for temperature cycling tank liner specimens, establish standardized test methods, and provide durability data on various materials. Permeability data will be used to develop an understanding of mechanisms for changes in liner permeability during thermal cycling. A test methodology for assessing liner behavior and durability with the liner attached to the composite reinforcement shell will be developed.



Question 1: Approach to performing the work

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

- The general approach to develop a testing method of thermal cycling and permeation measurement of polymer specimens is effective.
- The approach to develop a standard protocol for testing tank liners and then publishing the protocols and results is good. It is also good that Oak Ridge National Laboratory is conducting tests called for in existing safety standards for fuel cell electric vehicles (FCEVs), such as SAE J2579. Planned testing with specimens that are sectioned out of actual tank liners is much better than testing coupon samples. Planned testing of integral liner/composite overwrap samples is also good, although this will likely require adjustments to the test procedures/equipment and analysis. However, it is not clear how this approach differs from the methods being used by the tank manufacturers to qualify the tanks that they produce. The presentation did not appear cognizant of prior work in this area or of what testing is being carried out by the tank manufacturers. The project needs to ensure that there is minimal overlap and duplication.
- Using disks might allow researchers to be able to predict the materials properties for diffusivity in some conditions; however, it is likely not a good method to evaluate the performance of liners in actual systems. Liners in systems will be exposed to different flexural and tensile conditions as well as interactions with the surrounding walls, bosses, etc.
- The original approach was valid and continues today, but progress has been slow. The ability for the project team to overcome obstacles throughout this project has resulted in slow but steady progress. The approach needs to focus solely on developing and providing to the industry a testing technique that can be used soon by tank and liner manufacturers. This is a key technology but it is at risk of being surpassed by industry that is using less technical approaches such as submerged leak testing. The approach by industry will not gather key durability aspects such as the ones this project is developing. The effects of temperature cycling with the liner are very important and require a repetitive testing approach such as the one this project is working to develop.
- The name of the project refers to “Life Cycle Verification”; however, this project is dealing with permeation only. The tests are dealing with permeation based on temperature cycles at specific pressure levels. Other parameters (e.g., liner buckling) are not mentioned. The project team should describe which real tank operation parameter could have an impact on permeations and which one will be applied at the

tests and why. It is unclear what the worst case parameters are for permeation. One test operation point is 700 bar at -40°C. This is not a real tank operation point. It should be assessed if this could have an impact on the performance of the specimen. The expected potential failure mechanisms should be listed. It is unclear how these failure mechanisms are addressed. The impact of rapid depressurization on the specimen itself should be assessed (researchers should compare the depressurization rate during the test with real depressurization rates in tank systems).

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

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

- Given the size of the budget the team has made good progress, particular in addressing the high-pressure seal for different types of polymers.
- The accomplishments in fiscal year 2013 look to be the best accomplishments for any year of the project. However, the progress is very slow and after five years one would expect the barriers and obstacles to be overcome, especially when dealing with sealing issues for which there are experts in the industry who could assist.
- Much time and effort was spent on sealing the disks to the apparatus—this seems like a distraction to the overall goal of characterizing different liner materials. The process was very much trial and error—it was very laborious without much strategy. Consultation with tank original equipment manufacturers (OEMs) or other partners could have significantly helped to mitigate this effort.
- There are no measured permeation rates within the past five years (the project started 2008), based on the assumption that the plots in the backup come from the literature. There was no information given about progress (percent rate) on the “overview” slide.
- One finding that has emerged is that permeation appears to be dependent on polymer compressibility. This is an important finding because storage tanks will likely undergo many compression/decompression cycles during the lifetime of an FCEV. In addition, the temperature of the liner can vary in the extreme from -40°C to 85°C. The accomplishments are somewhat lacking because of difficulties with the experimental equipment, specifically, in getting a robust seal around the edges of the sample. There may be other delays ahead because of the need to accommodate integral liner/composite samples for testing.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.0** for its collaboration and coordination.

- The project team worked with other tank OEMs; however, the team did not seem to benefit from the OEMs’ knowledge in designing test apparatuses or understanding the critical areas of a tank where liners could have permeability issues (joints, bosses, etc.).
- A partner should be identified and contacted to review the general approach to measuring permeation.
- The project is important to the DOE Hydrogen and Fuel Cells Program (the Program) because it works to ensure the safety of compressed hydrogen storage on board FCEVs. Collaborations with tank manufacturers are mentioned but not enumerated. The project should interact with the manufacturers to ensure that the focus is on issues considered to be important by the manufacturers, even if permeation studies are not. Many tanks from different manufacturers have been in service for a number of years and permeation has not been reported to be a significant issue. Of more importance are the interactions between the tank and the liner under the extremes of ambient temperature and pressurization/depressurization cycles.
- The collaboration and coordination were not well articulated.
- It is not clear which Type 4 tank manufacturer has been involved in this project or how the manufacturer’s testing method is integrated into the project.
- There does not appear to be good collaboration. The collaborators listed are tank manufacturers, but they look to only be supplying liner samples. The real collaboration should be high-pressure test equipment manufacturers that can address the sealing issues and high-temperature fluid experts who can assist in the temperature cycling. None of these experts look to be consulted and thus progress is slow.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This is an important study to bolster the understanding of this particular subcomponent.
- The life cycle of polymer liners in high-pressure storage tanks is very important and critical for the industrial application of a practical hydrogen storage system.
- The permeation rate of the liner is one of the main performance criteria for a Type 4 vessel. The definition of the test procedure is also important, but it is not included.
- The project is important to the Program because it works to ensure the safety of compressed hydrogen storage on board FCEVs as they are introduced into the market. Many tanks from different manufacturers have been in service for a number of years and permeation has not been reported to be a significant issue. Of more importance are the interactions between the tank and the liner under the extremes of ambient temperature and pressurization/depressurization cycles. The project is wise to undertake some work in this area.
- This is clearly an important task in the development of improved liners for storage vessels. The principal investigator, however, was bogged down with a non-ideal test apparatus and seems to have lost focus on the end goal of understanding the overall system issues with the liners, not just material permeability.
- The relevance of this project is that it is developing a key technology that is truly needed by the industry. Liner durability is very important and is yet to be determined in a long-term storage system where high pressure and potential risk are present. As time passes, however, industry is advancing and the relevance is diminishing, so the slow progress is impacting the overall relevance of this project. It is important enough that it must be finished.

Question 5: Proposed future work

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

- The proposed future work follows from the work to date.
- The testing of the polymer liner with the interaction of fiber wrapping is very important. The team needs to come up with a practical method to do this.
- Researchers should review the test procedure before continuing with the tests. Three additional specimens are scheduled to be tested within the next five months (project end is scheduled for October 2013). This is an optimistic schedule.
- The project team should deemphasize the work on repeating tests with 350 bar—there is likely not as much to be learned because conditions are not as challenging. The team should also increase its emphasis on understanding liner interactions with composite layers in real tanks.
- The planned work for the remainder of 2013 and for 2014 is reasonable. The planned work on sectioned tanks is definitely needed to develop an understanding of the interaction between the tank and the liner. Understanding failure mechanisms would be an important contribution to the community. Where possible, testing should be carried out under “real-world” conditions or as close to those as possible given the limitations of the test equipment.
- The outlined future work is too broad. All efforts should be placed on completing the testing protocol and proofing the testing equipment. Testing other materials is much less important than actually delivering an accurate, repeatable test procedure and equipment. The one area of future work that does not belong in this project is the work targeted to understand the region between the liner and the composite as well as the hydrogen absorption in the composite. This is very important to storage vessel performance and a project needs to address this aspect, but not this project. This project needs to complete the testing approach and publish its work for industrial use.

Project strengths:

- The testing technique represents a good approach.
- This project features a good selection of materials and treatment.

- The team has a very good material level understanding of the polymer liner and how to quickly screen its cycling behavior.
- The test facilities appear to be very capable of producing quality results on test sections of liner materials. Hopefully, the equipment will be able to test actual tank sections in a similar manner either with or without modifications.
- The accomplishments in the testing protocol and apparatus are showing progress and could lead to a standard testing method that would be a key element for the industry. The strength of this project is that the outcome is important and appears to be relatively close to completion.

Project weaknesses:

- This project features a poor test apparatus and lacks a plan to translate results into overall system validation.
- The team has not shown a valid method of testing the interaction between the polymer liner and the fiber wrapping, which is very important for a practical high-pressure Type 4 system.
- Tank/liner interactions under extreme conditions may be a more important issue to examine than permeation. The presentation did not discuss past efforts to study permeation through tank liners or ongoing efforts by the tank manufacturers. It is difficult to determine possible overlap and duplication.
- The progress has been very slow and the lack of "expert" collaborators appears to be a root cause of this. The weakness is the appearance that the work was focused internally and that help was not requested from industry.
- More effort should go into describing plans to approach the study of delamination of the liner from the composite overwrapped pressure vessel (COPV) shell.

Recommendations for additions/deletions to project scope:

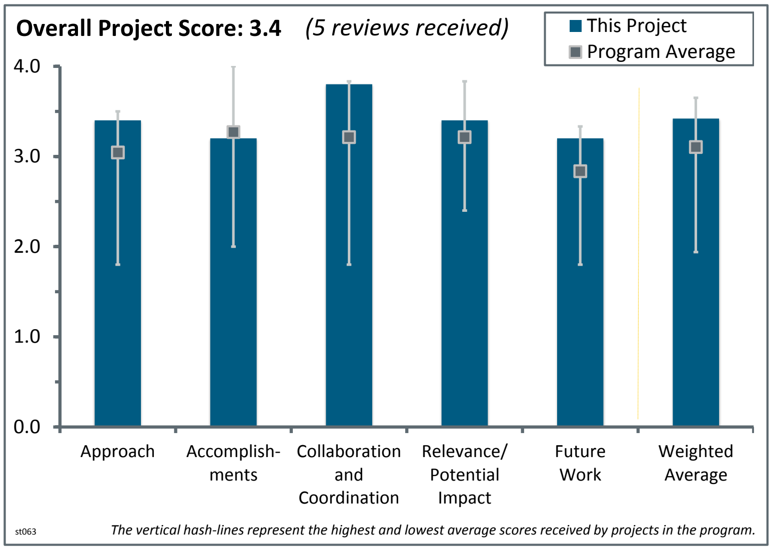
- The team should reevaluate the test methodology.
- The team should elaborate on how to study delamination of the liner from the COPV shell.
- The project should include the analysis of interaction between the polymer liner and metal joint at the cylinder neck, which accounts for a significant portion of the Type 4 tank failure mode.
- The research team should quickly establish a plan to understand areas of potential concern in different parts of the tank with regard to material durability (not just permeability) and test for those conditions where the material may experience additional stress.
- The project team should increase efforts in understanding tank/liner interactions under pressure and temperature cycling to the expected extremes in pressure and temperature. The project team should also look for new and novel tank liner materials for testing. A good outcome from this project would be establishing a standardized test procedure that could be used for qualifying liner materials in a consistent manner.
- The communication of a test procedure, standards, and results needs to be completed soon. These findings should then be given to a testing equipment manufacturer for collaboration on building a first-generation device. This work is important and the team needs to look outside for industrial partners to build a turnkey system and more aggressively overcome the obstacles, such as sealing and temperature control.

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, favorable thermodynamics, and kinetics fulfilling the U.S. Department of Energy (DOE) onboard hydrogen transportation goals. Specific objectives for the project include avoiding the impractical high pressure needed to form alane (AlH_3), avoiding the chemical reaction route of AlH_3 that leads to the formation of alkali halide salts, and utilizing electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH_3.



Question 1: Approach to performing the work

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

- This project has made progress in some key areas over the past year. Most notable are the development of a closed cycle involving regeneration of metal alanates ($MAlH_4$) to serve as a source of AlH_3, and the production of high-purity alpha AlH_3, as evidenced by powder x-ray diffraction.
- This project is positively evolving toward what could likely be a practical regenerable AlH_3 process that would be important as a hydrogen storage source for fuel cell electric vehicles and to numerous other near-term fuel cell applications. Because the process is electrochemical, its broad scalability may prove to be very important.
- The research team has sharpened the focus of the approach over the last year. Now it is well focused on chemical efficiency. The approach is also being better communicated. It is unclear whether the approach should include defining which of the many half reactions shown are operating under regeneration conditions.
- The project is moving in the right direction toward AlH_3 regeneration. So far, the researchers have been able to increase the reaction rate of AlH_3 regeneration by increasing the conductivity during electrochemical regeneration. Likewise, the researchers have investigated barriers to this process by examining morphologies of the product phase. They have been able to avoid the formation of Li_3AlH_6 dendrites that short-circuit pathways during the regeneration reaction by changing the cell geometry. Although this is not one of the stated goals of the research, one of the useful project outcomes is that the investigators also suggest a reaction pathway to regenerate $LiAlH_4$.
- The research group utilized electrochemistry combined with organic and physical chemistry to develop new experimental approaches for cycling the Al-AlH_3 system in a solvent. There is a strong focus toward closed materials cycles and obtaining high actual measured energy efficiency. The number of partners is suitable compared to the amount of funding, and each partner brings in different expertise. The approach is a more direct conversion of renewable electricity to chemical energy and has a huge potential for possible applications, both mobile and stationary.

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

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

- Good progress has been made in several key areas.
- Aluminum is abundant and cheap, and its hydride contains large and usable amounts of hydrogen both measured volumetrically and gravimetrically. The research consortium has already discovered a new catalytic approach that increases the yield of AlH_3 and provides higher electrochemical cell efficiency.
- With a small amount of funding, the team continues to make progress that impacts overall AlH_3 regeneration efficiency and cost. Finding ways to improve cell conductivity has led to improvements in AlH_3 production rates. The team has produced prototype cell designs that demonstrate mitigation of dendrite formation. It also demonstrated $LiAlH_4$ electrolyte regeneration, albeit at an 80% recovered yield—there is room for improvement here.
- The team has successfully addressed issues with the reactor evolution as they arose. Key features include the highly saturated electrolyte that enhances the precipitation of AlH_3 adduct to aid in physical recovery. Additional important accomplishments include the move toward a separator such as Nafion, tripling electrolyte conductivity, and regenerating the electrolyte.
- The investigators are clearly making progress toward their stated goals (and those goals are aligned well with the DOE goals). For example, the investigators have developed alternative designs to the electrochemical reactor based on the formation of deleterious products (e.g., Li_3AlH_6 dendrites that caused short circuits in the prior reactor design). Product yield, cost, and safety were considered during the development of the regeneration process. However, the work lacks discussion of AlH_3 regeneration reaction rates (as a function of cell voltage). This is also an important consideration for practical applications of this electrochemical approach.

Question 3: Collaboration and coordination with other institutions

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

- Sensible collaborations have been established with key institutions and laboratories. These collaborations are well managed and appear to contribute in a meaningful way to the overall project.
- The investigators list collaboration with two other institutions on slide 3 (i.e., Brookhaven National Laboratory [BNL] and the University of Hawaii), but all of the technical accomplishments described were performed at Savannah River National Laboratory (SRNL). The investigators suggest the development of new, industrial collaborations on slide 21.
- This project is very well coordinated. The number of collaborators is relatively small. The information on the poster indicates that there are already new discoveries that will be patented.
- The project shows good coordination among current and past efforts in AlH_3; the project team has a good handle on where the state of the art lies. The project may improve if some communication occurs between the Argonne National Laboratory (ANL) systems modeling effort to ensure that the research priorities are set appropriately with the small amount of funding available.
- It is unclear how responsibilities are exactly shared among collaborators.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The successful development of a low-energy electrochemical route to AlH_3 from aluminum and hydrogen gas would redefine the whole direction of the Hydrogen Storage program going forward.
- This project has a huge potential for future high-energy-density storage. The actual, measured energy efficiency of 68%–75% has already been achieved and is approaching the ideal value of 83%. The project approach has great novelty, specifically in employing direct electrochemical energy storage.

- Chemically and energy-efficient regeneration of off-board regenerable materials is highly relevant to DOE RD&D objectives to reduce the cost of off-board regenerable hydrogen storage systems. The potential impact of this project is high if a well-integrated, chemically efficient, and energetically efficient process can be defined and demonstrated in the laboratory.
- Because AlH_3 has a 10 hydrogen wt.%, this approach creates a pathway to onboard storage that can be potentially critical for hydrogen's success in transportation. The methodology also creates significant technical opportunities in many other fuel cell applications that may see commercial growth in the nearer term than the fuel cell electric vehicle.
- Because AlH_3 is one of the most promising metal hydrides for meeting DOE's targets, the goal of low-cost regeneration is extremely relevant. The researchers have demonstrated that the electrochemical regeneration approach being developed is also relevant to other hydrides (e.g., $LiAlH_4$); however, a cost comparison with other methods to form $LiAlH_4$ has not been made. Such a comparison would have been useful to demonstrate that the electrochemical approaches, when generalized, are beneficial across a variety of hydride systems.

Question 5: Proposed future work

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

- The proposed work for the coming year is sensible and builds on this year's progress.
- The future work (slide 21) is detailed and lists items that seem to be both measurable and achievable.
- The improved electrochemical cell design and AlH_3 separation are very important to realizing the potential of this process.
- It would be very interesting to investigate the possibilities for scaling up the synthesis to obtain, for example, 100 g AlH_3.
- The proposed future work contains a significant amount of work to accomplish at SRNL for only $400,000. The project has shown success in providing proof of principle. The principal investigator (PI) should consider whether to continue to invest in improving cell designs or instead focus on areas that have potentially more impact on overall efficiency/cost issues, such as separations (of AlH_3, of catalyst components, etc.), and the recycle of aluminum from spent fuel to anode formation. Feedback from systems analysis experts would be helpful here. It is unclear whether the future work should anticipate another round of "cost estimation" by ANL. If so, then the researchers may want to prioritize future work to address process cost estimation needs in concert with ANL input. For example, the impact of the future work may be improved by considering how the returning aluminum spent fuel enters into the regeneration process; for example, how one takes spent aluminum to form the anode efficiently. The future work might profit by including tracing where the "dopant" in AlH_3 ends up, and how/when/if it needs to be separated from the process and recycled.

Project strengths:

- This project features a genuinely original approach to a challenging technical problem.
- The project partners collaborate well and efficiently, as demonstrated by the amount of results already achieved and in light of the modest amount of funding.
- This project is focused on overcoming a significant barrier to off-board regenerable hydrogen storage materials.
- This project features a knowledgeable and capable team, a Cooperative Research and Development Agreement (CRADA) with an industry partner, and a good semi-empirical approach.
- The project lays a platform for developing electrochemical methods for AlH_3 regeneration (and organic adduct removal). If this can be done efficiently, this is a relevant goal for meeting DOE targets. The approaches taken involve engineering (reactor design) and materials science (understanding the role of morphologies in the product phases formed). Clearly, this team of researchers is capable of driving the project toward the end goal of low-cost and efficient AlH_3 regeneration.

Project weaknesses:

- The project would likely be helpful with more focus on the actual mechanism for electrochemical hydrogen uptake and the function of the additive/catalyst. It is unclear if there are some intermediates involved; for example, similar to those suggested for the alanate system (Al_2H_7). However, that may require increased funding support.
- It is still not clear how much real assistance is provided electrochemically to the reaction MH + Al + $1.5H_2$ = $MAlH_4$. This reaction was shown to work perfectly well using conventional energy inputs (temperature/pressure) both by Dr. E.C. Ashby at Georgia Tech in the ‘60s, and more recently by Dr. Jason Graetz at BNL.
- The project could be improved by incorporating input from systems analysis to focus the limited resources on highest priority topics.
- There is a clear lack of participation by the collaborating institutions (i.e., BNL and the University of Hawaii).

Recommendations for additions/deletions to project scope:

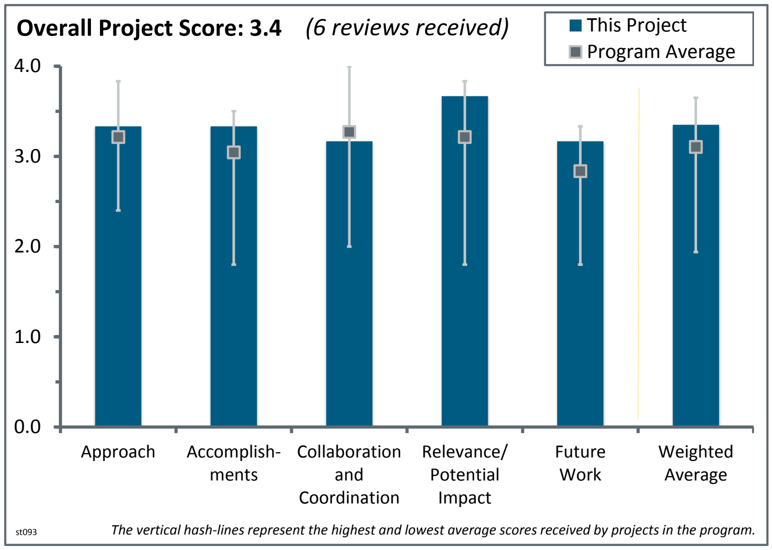
- The project began with a focus on AlH_3, and has shown a lot of progress in that regard. However, the electrochemical methods being developed here for AlH_3 may be more generally applicable to other light metal hydrides. An analysis and further thought/comment about the cost benefit to applying this process to other hydride systems would be useful.
- The research team should follow the proposed plan; utilization of a “low-boiling-point” solvent (DME) may be more efficient for the synthesis of AlH_3, along with further optimization of the activation process for aluminum and utilization of efficient additives/catalysts. The team should also investigate the possibilities for scaling up the synthesis to obtain larger amounts of AlH_3.
- Given the limited dollar resources this project has, it may be helpful to focus prioritized areas on systems analysis feedback. Because proof of principle of cell design has been demonstrated, perhaps postponing/delaying the improvement of the electrochemical cell design activity would provide more resources to focus on separations issues, for example. Separations tend to be the most costly portion of integrated chemical processes.
- The project team may also want to look into Zirfon as a cell separator. It is a separator used in many alkaline electrolyzers. It is zirconia particles in a polysufone matrix. THF, like the DME used earlier, is highly flammable. Its auto-ignition temperature in air is 321°C; this is not expected to occur unless an anomaly happens in the cell to raise the temperature or create a spark in the presence of air. This is unlikely, but it may lead to scale-up and production-level codes issues. It is unclear if any more benign solvents have been considered. The overpotential cited on slide 9 is for the specific experiment and its design. It is unclear if there is design latitude for reducing it. In a commercial system, the cell design will be driven at some aerial current density and should have an ohmic varying with current density. This may contribute to higher fractional energy consumption. It may be worthwhile to add an effort to understand the cell design and current as a function of energy consumption to optimize the efficiency.

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 objective of this project is to reduce the manufacturing cost of high-strength carbon fibers (CFs) by means of significant reduction in the production cost of the polyacrylonitrile (PAN) precursor via hot melt methodology and the utilization of a polyacrylonitrile-vinyl-acetate (PAN-VA) polymer. This technology has the potential to increase the throughput in the production of the PAN precursor and decrease the cost of precursor production.



Question 1: Approach to performing the work

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

- Because the precursor is the main cost driver of a CF vessel, it is a very good idea to investigate a different production process.
- The team is effectively addressing barriers as they are discovered. The project is as well designed as it can be for the large scope and associated limited funding. Demonstrating a compelling reduction in manufacturing cost does not appear feasible during the remaining period of performance. The team's integration with other efforts is consistent with work being performed and is acceptable.
- The approach for this project is well focused. The analysis of former work by BASF has led to a refined approach that addresses the issues and concerns of the previous work. Much work has been accomplished in fiscal year 2013 as a result of the focus that this project contains.
- Melt processing of a PAN precursor is projected to result in lower cost precursor fiber than is currently produced by solution processing. The approach is simpler and more environmentally friendly than the current process. The approach is to improve the PAN melt stability by reducing the temperature below the degradation temperature. The approach builds on the past work by BASF that was abandoned for economic reasons. Because the impact of small changes in processing conditions is not easily predictable, a high level of experience and expertise in polymer processing is required to investigate the process space in a reasonably efficient manner. The team excels in this area.
- The overall approach of the project is good because it pursues the melt-spun processing as an alternative to the solution processing. The approach could be improved by including quantified metrics for evaluating the fiber surfaces rather than simply a subjective assessment. It would also be appropriate to cross-section the fibers to evaluate the internal porosity rather than just on the surface. Additional information on the steps that were used and could be used to improve the fiber properties would add value to the approach in order to highlight the science rather than the "art" of the processing. The project should transfer to a polyacrylonitrile-methyl acrylate (PAN-MA) rather than a PAN-VA because the properties will not be achieved with the PAN-VA. Finally, a cost model needs to be developed in the near term to confirm the potential savings of the process. The previous cost estimates were from a study from five years ago and need to be updated.

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

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

- The accomplishments are good, especially the significant improvement in mechanical properties. The progress provides a step toward gaining confidence in the feasibility of the melt-spun processing precursor. It would be useful to quantify the specific cause and effect that facilitated the progress.
- The conversion of a current sample into CF results in a tensile strength of 150 ksi. Current aerospace-grade CF used to manufacture tanks has a tensile strength of approximately 700 ksi. The project is on a good path, but it is not clear whether tensile strength values (approximately 700 ksi) will be reached. The addressed barrier is the high cost of CF. It is stated that the production cost can be reduced by 31%–33%. However, there is no correlation to the DOE vessel target costs.
- The project achieved significantly greater progress than last year. The Oak Ridge National Laboratory (ORNL)/Virginia Tech (VT) team produced PAN CF that has very good outside surface characteristics with no detectable damage, notching, or cracking. Numerous trials met or surpassed their March milestone of 15 Msi modulus and 150 ksi strength. This progress was possible because of the concerted efforts of ORNL and VT to modify precursor chemistry and processing conditions in an effective manner. The fact that some of the success was fortuitous does not diminish the accomplishment.
- The accomplishments over the last year are impressive, with key advancements made in the spinning, post-spinning treatment, and carbonization of the fiber. The improvements to the pressure chamber and winding mechanism are very good and the incorporation of the steam stretch has resulted in a very good VA-based precursor, as noted in the scanning electron microscopy analysis. The “outstanding” rating suggests that barriers “will” be overcome. The progress over the last year would easily be rated as “outstanding,” but scale-up barriers still exist and need to be better addressed.
- After somewhat slow progress in previous years, this project has made some nice advances this year.
- Progress has most certainly been made in advancing this potentially impactful work, but an unequivocal connection to DOE goals is unclear.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration between ORNL and VT is very effective and helped the researchers overcome some significant obstacles this year.
- The degree to which this project interacts with other entities and projects has been dictated by necessity and is optimized for the work and limited funding available.
- Collaboration is mainly between ORNL and VT, which is important because of their individual expertise. With some initial success, additional manufacturers have been approaching ORNL; further collaborations could increase the chances that the process will be commercialized.
- It is understood that this project is dealing with a very specific technology; however, more partners would be preferable. Please continue looking for more partners.
- The collaboration with VT seems to be useful, but further collaboration should be considered with a U.S.-based chemical or fiber company that could assess the potential of the melt-spun processing for a commercial precursor. A chemical company partner could also assist in the development of a realistic cost assessment based on its knowledge of capital and operational costs, or another cost consultant should be added to the project.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Because CF is the main cost driver, this project has a high potential to reduce CF costs significantly.

- While still at risk of success, the potential relevance is extremely high to the DOE Hydrogen and Fuel Cells Program (the Program) goals and objectives.
- The project is very relevant to the Program because early fuel cell electric vehicles will use compressed hydrogen storage systems. Lowering the cost of CF is crucial to the success of the vehicle launch. Lowering the cost of precursor fiber is a step in the right direction, but lowering the cost of carbonizing precursor fiber into finished fiber is also needed.
- The project is highly relevant because it is focused on the main cost factor (precursor) associated with the CF, which is clearly the highest cost driver in the compressed hydrogen tank system. The potential cost saving of 31%–33% would have a high impact on reducing the cost of the tank system and fuel cell vehicles. However, an updated cost model is needed to confirm the potential savings.
- This project is focused on meeting the cost-savings target of the Program. It is not addressing, however, the increasing movement toward a higher-strength CF. The technology that this project is developing is a key component of addressing a lower-cost CF, but it may not be well positioned to meet the needs of the Program. The importance of this project cannot be understated, because its successful development will certainly make a commercial impact in the use of CF.

Question 5: Proposed future work

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

- It is crucial to see how properties and cost/process change with use of methyl acrylate.
- The project has naturally experienced barriers commensurate with developing a manufacturing process and material. The planning has been as logical as allowable with such an endeavor. For this reason, it is acceptable that discrete decision points are lacking; there has been and will continue to be discovery. Equally commensurate with this type of effort was not knowing the alternate pathways in advance, but this did not stop the team from addressing issues as they encountered them.
- The tensile strength target is 600 ksi. The tensile strength target should be comparable with CFs that are currently used in a 70 MPa system (i.e., 700 ksi). It is unclear if 600 ksi is enough to manufacture a 70 Mpa Type 4 vessel.
- Future work plans for the remainder of 2013 focus on scalability and increasing mechanical property values. Alternative co-monomers, particularly methyl acrylate, need to be investigated; the project team has listed this area for future work.
- The general plan for future work was provided, but the specific plan for improving the strength would be useful. The ultimate goal would be to produce a low-cost carbon composite that should include an assessment of the fiber with the resin to ensure the translational strength. A high-level cost assessment should be included to verify the main benefit of the project.
- The future work for this project continues to address the barriers associated with melt spinning. However, more effort could be placed in optimizing the pressure chamber and spinning process, as well as developing an in-line steam stretch and treatment process. A fully integrated process is a critical step in being able to develop a commercial process. The future work is also aimed at improving the CF properties, but it falls short in being able to afford the necessary time to optimize the carbonization process for improved properties.

Project strengths:

- The greatest strength of this project is in its potential impact on DOE goals and the proof of progress that the project team has made.
- This project’s strengths are the project team’s extensive knowledge and expertise in CF production and polymer processing and the excellent facilities for producing CF.
- The project is focused on the key cost driver for compressed hydrogen tanks and is making good progress with the mechanical strength properties.
- The collaboration between ORNL and VT and the accomplishments in the last year are notable and represent the strengths of this project. The approach and passion of the principal investigator are also strengths.

Project weaknesses:

- The project's weakness is inherent in the scope of work that was proposed and the inherent risk typical with the level of manufacturing and material development required for quantifiable success.
- The project team needs to explain additional aspects of the science rather than the "art" of the process. The team also needs to update the cost estimate based on the current assumptions.
- The relation between the properties of the precursor and the finished CF is not clear. Understanding fundamental materials properties and their relationship is beyond the scope of this project. The project will have to rely on repeated trials to define the process conditions to ensure acceptable CF performance.
- This project is making substantial headway but appears to be significantly underfunded. This is important work and the funding does not fully provide adequate access to resources and time to fully develop this precursor.

Recommendations for additions/deletions to project scope:

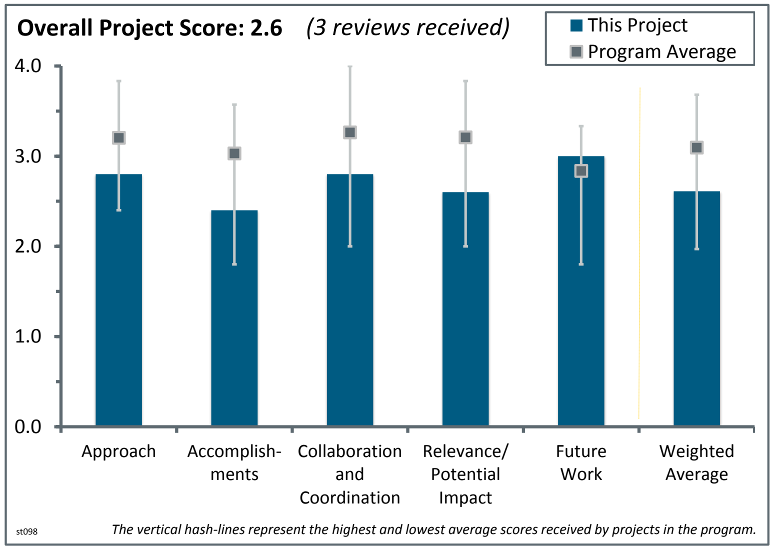
- The project team should continue to seek industrial collaborators to provide process knowledge and facilities.
- There is certainly no recommendation to de-scope in terms of funding. However, it would be good to see a re-expression of metrics and a clearer roadmap to reaching DOE's goals. A breakdown of manufacturing costs and associated risks with each step would help in evaluating progress and focus.
- The project team should add a partner or effort in the area of cost estimating—it should consider including a consultant or an individual in the fiber industry to ensure that precursor development will have a high potential of delivering the needed attributes for a commercial high-strength fiber.
- The project team should consider a better application within the DOE umbrella where additional funding can be made available. The impact of a successful project in expanding the use of CF in industrial and automotive applications could be substantial. Efforts to light-weight automobiles could benefit from this project more than the Program could. DOE should provide the necessary funding to more quickly and thoroughly develop this precursor.

Project # ST-098: Development of a Practical Hydrogen Storage System Based on Liquid Organic Hydrogen Carriers and a Homogeneous Catalyst

Craig Jensen; Hawaii Hydrogen Carriers, LLC

Brief Summary of Project:

The objectives of this project are to identify the most versatile liquid organic hydrogen carrier (LOHC) for hydrogen storage and to design an LOHC containment system to interface with a fuel cell. The LOHC chosen should give the best combination with the pincer catalyst for high cycling capacity, rapid dehydrogenation kinetics, and no degradation of LOHC upon cycling. The LOHC tank and reactor system should be space-, mass-, and energy-efficient and should facilitate hydrogen release through an easily interfaced connection to a fuel cell.



Question 1: Approach to performing the work

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

- The project has taken a logical, well-planned approach to this problem. The investigators should have looked at possible advantages that could have been achieved by using single isomers (i.e., cis vs. trans hydrogen addition across double bonds). Theoretical calculations could quickly show if improvements would be possible by using a single isomer.
- The project is generally well designed and addresses the U.S. Department of Energy (DOE) goals and barriers. Liquid carriers are likely to offer balance-of-plant and infrastructure benefits, especially compared to solid chemical hydrides.
- The approach to hydrogen storage using reversible, low-temperature, and pressure liquid organic carriers addresses several barriers that currently exist for onboard storage of hydrogen. In particular, liquid regenerable systems could, in principle, provide many advantages to an engineered system. The project is focused on proof-of-principle demonstration using low pressure, 1 bar experiments for the release of hydrogen from a low-capacity carrier.
- This is a unique project that is designed to test the benefits of using homogeneous catalysis in liquid carriers. The catalyst would be carried in the liquid and used to release hydrogen as well as regenerate hydrogen. It might not meet the vehicular targets, but the insight developed here could benefit near-term market strategies of the DOE Hydrogen and Fuel Cells Program (the Program).
- The approach is to develop catalysts for dehydrogenating organic compounds. There is no originality in this work. The researchers are using well-established organic compounds that are basically the same as what is in the big Air Products patent. They are using a catalyst developed by the Jensen group a number of years ago. They are interacting with General Motors (GM) and are considering the engineering issues with their approach. They have the catalyst loading down to 100 ppm, which is good because they are using a rare metal, iridium, as the catalyst. It would have been good to see an attempt to use a catalyst based on a first-row transition metal. The helical reactor is very nice. It would have been good to see a cost analysis of the catalyst. The bladder storage tank is nice. The researchers are developing a liquid chemical hydrogen storage fuel.

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

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

- The researchers have made good progress toward meeting their goals. They have not completed their catalyst cycling studies, but good progress is being made. It is unclear whether they can scale this process up and whether they can meet the weight percent needed to be viable. The 100 ppm level for the catalyst is a real accomplishment.
- This project has not shown a great deal of progress over what was shown the previous year. Notable progress was found in the area of identifying LOHCs that are liquid in both hydrogenated and dehydrogenated forms. Dehydrogenation rates were termed “adequate,” but they took 18–20 hours to run to completion. This time to completion seems at odds with the characterization “adequate.” The experimental apparatus limited dehydrogenation kinetics studies to around one atmosphere; these are conditions not on par with DOE requirements for the inlet pressures of hydrogen for fuel cell applications. The recyclable capacity was not demonstrated. While expected to be low due to material ultimate capacity limitations, such a demonstration would have been valuable.
- Accomplishments this year have gone some way toward DOE goals, but a substantial gap remains. The volumetric and gravimetric capacities remain at the levels of prior years for this project, and although another catalyst and several LOHCs have been tested, no new systems appear to have been developed. The rate of dehydrogenation of BPHP may be faster than other compounds tested, but this still takes 20 hours at 13 degrees below the boiling point. It is unlikely that this compound will present a practical LOHC. The measurements of hydrogenation rates (with a 100 ppm catalyst) and the commencement of cycling studies show useful project progress.
- Despite determined efforts and a good approach, no viable combination of chemical hydride and pincer catalyst was found.
- It was obvious, appreciated, and appropriate that the principal investigator (PI) and coworkers used cost as a primary “filter” for the liquid carriers they considered. They appeared to eliminate a number of potential materials based on the cost of the material on a gram basis from a research chemical supplier. As the project is coming to a close, it would be valuable to have a similar cost analysis for the catalyst. Even if it is based on “Aldrich” costs, it will be valuable for others that come along after and consider homogenous catalysts for liquid carriers. The reviewer tried to estimate a back-of-the-envelope cost, assuming one used a 100 ppm iridium catalyst. One hundred ppm is 0.01 mol %, assuming 100 ppm is on a mole basis. For the liquid carrier used in the present study using MPHI, the researchers were able to get 2.9 wt.% hydrogen. For a 5.6 kg usable hydrogen system, they would need about194.6 kg MPHI (1,400 moles MPHI) at 100 ppm; this would require approximately 0.14 moles of catalyst. For the pincer catalyst, this is about 60 grams of catalyst. If this is incorrect, the researchers could provide a worksheet to provide the grams of catalyst required for a tank of fuel. There is some confusion over the turn-over number (TON); it is listed as 250–300 on an earlier slide (perhaps slide 8), and then the later slides suggest a TON of 100,000. It is unclear what the differences are in the two experiments. A TON of 300 is not so good for an expensive catalyst. A TON of 100,000 is excellent and one might get about 1,000 fills for the lifetime of the catalyst. One could spread the initial cost of the catalyst over the number of fills expected for the lifetime of the system. Also, detailed information is needed on how to get from an experimental rate to a “practical rate.” The Arrhenius parameters give a rate of 4x10-6 moles of H_2/s at 180°C. A “practical rate” is assumed to be five orders of magnitude greater—about 0.4 moles of H_2/s. It is also notable that the regeneration stops at approximately 89%. Perhaps this could be due to an established equilibrium (LQH2 = LQ + H2). This might start to answer one reviewer’s reoccurring question about what the conversion is at 5–10 bar back pressure in a system for a fuel cell vehicle.

Question 3: Collaboration and coordination with other institutions

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

- The internal collaboration between Hawaii Hydrogen Carriers (HHC) and GM looks to be excellent, with both sides closely interacting. No other external collaborations exist and such collaborations could be helpful.
- The work seems mostly confined to the PI's institute and subcontractor, and there does not seem to be any outcome evident from the interaction with Oregon State University (OSU). An additional collaboration with the Hydrogen Storage Engineering Center of Excellence (HSECoE) has been leveraged to help with the reactor design and modeling.
- The collaboration with the GM PI seemed good on the surface. The communication between HHC and GM may not have been ideal because it is hard to fathom how a member of DOE's Storage Tech Team and a member of the HSECoE apparently did not communicate the desired engineering-based technical targets or requirements (rates, pressures, etc.) to the HHC team members.
- It is understood that the reactor modeling effort by GM was reduced this past year, but it was not very clear how the collaboration with OSU is working. The connection is unclear.
- There is limited collaboration. The researcher should have engaged with Air Products, which has extensive experience with these systems.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.6** for its relevance/potential impact.

- This project features a good, honest appraisal of using a homogeneous catalyst with liquid organic carriers.
- The project aligns with DOE interests. It is not an exciting project because it does not involve the use of new material or of a new catalyst. It is hard to see it having an impact on chemical hydrogen storage, but it was good to learn if this approach will have an impact or not.
- The approach this project took is in principle highly relevant, and liquid reversible materials offer many advantages to an engineered hydrogen storage system. The project's relevance suffered by not adhering to basic materials and testing requirements for release systems. Project outcomes would have been easier to judge had experiments been conducted at conditions relevant to DOE's technical requirements for fuel cell operations.
- Although the project is highly relevant to the goals and objectives of the Program, the potential to significantly advance progress does not appear to be strong. The project is nearly complete and many of the metrics (especially capacity and rate of release) remain short of DOE targets.
- None of the materials studied had any real potential for meeting Program targets.

Question 5: Proposed future work

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

- It will be very helpful to others thinking about this approach to see a mini-analysis of homogeneous catalysis in liquid carriers. Some more relevant chemical engineering input is needed; specifically, how "100 ppm," a "TON of 350–100,000," and "practical rates" translates to a system. A simple Excel spreadsheet could be used, where one could input the molecular weight of the organic carrier and the wt.% hydrogen (to know how 100 ppm of catalyst is converted to moles and grams of catalyst and how many liters of liquid carrier are required for 5.6 kg of usable hydrogen). Also, the optimum TON for a homogeneous catalyst at 100 ppm is unclear. Three hundred and fifty is likely too small and 100,000 is likely more than necessary for 500 fills of 5.6 kg hydrogen. One might add these liquid carriers to the DOE database of materials and include rate information in order to determine how much liquid carrier is needed at what temperature to give a rate of 0.2 g H_2/s. It seems like this analysis would help this team as well.
- The project is essentially complete and the researchers are finishing the cycling studies on the catalyst. The modeling of the process and reactor at GM is being completed.

- This scoring section is not applicable because the project is very near completion.
- The proposed future work is not rated; the project is ending.
- Not applicable—the project is complete.

Project strengths:

- This project features a potentially relevant approach.
- Despite being short of DOE targets, the project has developed some of the best-performing reversible liquid compounds for hydrogen storage.
- This project's strengths include its use of known chemistry and its liquid fuel. The researchers have substantial experience with the chemistry. There are good interactions within the team, including having GM on the team. The catalyst loading and performance are reasonable. The helical reactor is nice. There is good modeling at GM.

Project weaknesses:

- The HHC project team did not have experimental facilities to demonstrate hydrogen release under relevant conditions.
- This project contains chemistry and technology that is not really exciting. It is unclear if the researchers can meet the weight percent requirements, what the real cost and lifetime of the catalyst are, and what it costs to regenerate the catalyst.
- The terms "practical" and "acceptable" appear to be used without justification regarding rates of both hydrogenation and dehydrogenation. The examples given take several days for either process, which hardly seems "practical." The project should have defined what it meant by acceptable rates, tied these to DOE goals, and shown numerically how these were met.

Recommendations for additions/deletions to project scope:

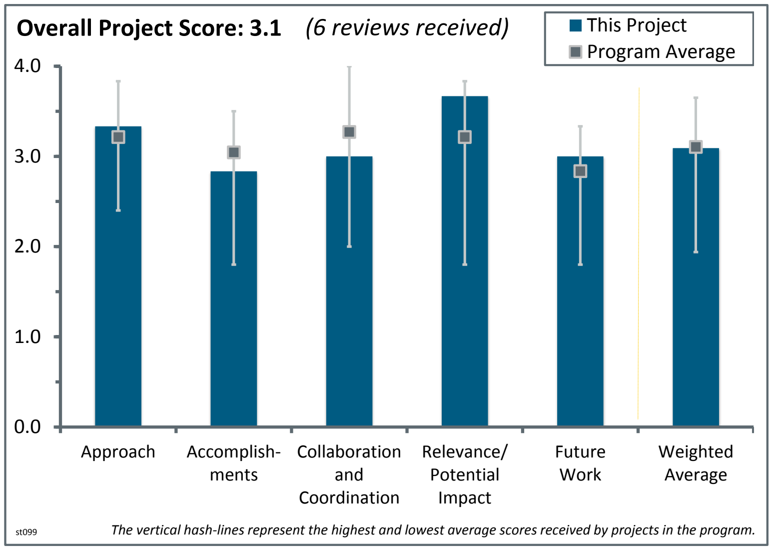
- This is not relevant because the project is near the finish date.
- There are no recommendations because the project is almost complete.

Project # ST-099: Development of Low-Cost, High-Strength Commercial Textile Precursor (PAN-MA)

Dave Warren; Oak Ridge National Laboratory

Brief Summary of Project:

The objective of this project is to develop a polyacrylonitrile-methyl acrylate (PAN-MA) formulation produced in a textile mill with as few changes to the precursor manufacturing as possible to achieve the performance requirements for hydrogen storage while preserving the high-rate, high-volume cost advantages of a textile mill. Carbon fiber (CF) composites make up 60%–80% of the hydrogen storage system, and the cost of the fiber accounts for the majority of the storage system cost. This project works to develop lower-cost precursors to meet performance requirements while preserving high-production-rate cost benefits.



Question 1: Approach to performing the work

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

- The approach of using a low-cost commercial textile precursor is good. The project benefits from two previous projects funded by the U.S. Department of Energy (DOE) Vehicles Technologies Office.
- The project is well designed, shows feasibility, and appears to be integrated with other efforts. The project has a compelling approach to reducing the cost of CF.
- The overall approach is sound; development of low-cost fibers is essential for decreasing the cost of CF and, subsequently, the cost of high-pressure hydrogen storage tanks that rely on CF overwrap. The project leverages previous work done under the Vehicle Technologies Office to produce lower cost CF for vehicle structural members. Oak Ridge National Laboratory (ORNL) is working with a manufacturing partner, FISIPE, that brings manufacturing capability and expertise from the textile industry. This may result in the development of a potentially lower cost route to CF. The project hopes to improve the properties of the precursor and the manufacturing throughput to lower CF cost.
- It was a good idea to continue the work of two former projects. However, because a CF for 70 MPa systems was not the focus of the former projects, it will be difficult to reach the goals for a 70 MPa vessel.
- The overall approach of the project is good because it pursues a textile-based precursor as an alternative means to reduce the cost of CF. The approach could be improved by including quantified metrics for evaluating the fiber surfaces rather than simply a subjective assessment. Additional information on the attributes to quantify a quality fiber would be useful in order to highlight the key characteristics. Finally, a cost model needs to be developed in the near term to confirm the potential savings of the textile precursor for an aerospace CF.

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

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

- The project accomplishments since the 2012 DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) have been significant. The most promising precursor formulation was selected based on test results. Carbonized fiber properties up to 400 ksi tensile strength and 30 Msi modulus were achieved. The major

issue with fiber "fuzzing" was resolved by FISIPE by modifying the precursor manufacturing process. Delays in receiving precursor material from FISIPE delayed the optimization of the final oxidation step by about four months.
- It seems that the project is on a good path, but it is not clear if the expected tensile strength will be reached. There is no information about the expected mass and/or cost reduction. The team should add these numbers and correlate them to the DOE targets.
- The F2000 precursor was down-selected as the sole precursor for further development (down from three as of fiscal year 2012). This precursor has gone through four of the seven steps that convert precursor to final fiber. Two major issues encountered in previous years were resolved (or partially resolved); they were related to the size uniformity of fibers and shape deviation from "round fiber." These problems underscore the importance of managing variability in fiber manufacturing because unintended variability reduces the effective strength of the CF.
- The team is making measurable progress toward DOE goals, which suggests that it is continuing to address the barriers encountered. Performance indicators were clearly presented in the form of attribute and cost impact. As is typical with most development projects, mitigation of barriers prior to them appearing was not feasible, leading to some delays.
- The accomplishments are good but the progress was not clear in the AMR presentation. Many of the same issues and down-selection accomplishment highlights were included in last year's presentation. The current status for the fiber strength is slightly better than the previous year. A significant gap still exists regarding the strength requirements for aerospace fiber. The optimization effort is encouraging because it shows that further steps can be taken. It would be helpful to have further information regarding the potential of developing computational models to further improve the optimization in order to reduce the physical testing.

Question 3: Collaboration and coordination with other institutions

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

- It seems that the project is in contact with all relevant partners.
- ORNL partners with FISIPE of Portugal. There is no collaboration with any partner in the United States.
- The collaboration with the precursor source has had challenges, but these have been well addressed.
- ORNL is partnered with FISIPE, which is headquartered in Portugal. FISIPE is responsible for precursor formulation and precursor spinning using textile-based processes. SGL Group recently purchased FISIPE and is a major CF producer. FISIPE is cost sharing by funding necessary plant modifications to produce the PAN-MA precursor by an air-gap spinning process. The role of SGL Group in this project is not clear.
- Because SGL Group has bought FISIPE, the collaboration is a concern. The project was delayed due to the formation of this relationship by four months. The future effect of the FISIPE integration into SGL Group is uncertain regarding the support for the project and the ongoing potential of commercializing the precursor.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Success of this project would significantly advance progress toward DOE RD&D goals and objectives.
- CF is the main cost driver of a pressure vessel, so this project has the potential to reduce cost and mass.
- Reducing the cost of CF is one of DOE's objectives for a 700-bar hydrogen storage option. Successful development of a low-cost commercial textile precursor can potentially help in meeting the DOE cost target for CF.
- Developing lower cost CF based on textile precursors is very relevant to the efforts of the DOE Fuel Cell Technologies Office to develop the technologies to enable the market introduction of fuel cell electric vehicles. CF accounts for about 65% of the cost of a CF overwrapped storage tank. Significant reductions in the cost of CF would enhance the prospects for commercialization.

- The project is relevant because it is focused on the main cost factor (precursor) associated with the CF, which is clearly the highest cost driver in the compressed hydrogen tank system. The potential cost saving for the textile precursor was not specified, so the potential impact can only be speculated for a compressed hydrogen tank. An updated cost model for the aerospace fiber is needed to confirm the potential savings.

Question 5: Proposed future work

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

- The plans appear to be logical and based on previous results.
- Given the technical issues encountered over the past two years, the future plans appear to be reasonable. It is very important that variability in fiber size and shape be reduced as much as possible.
- The goal of this project is to manufacture a fiber with 650 ksi. This is a little bit lower than a T700 CF. Tank manufacturers should be asked now if this tensile strength is sufficient to build a 700 bar vessel.
- Future work plans are logical and seek to maximize the material properties in the conversion protocol through refinements in time, temperature, and tension. Other possibilities mentioned in the presentation, but not in the scope of the project, include investigating existing sources of precursor materials and possibly developing a new precursor supplier.
- The general plan for future work was provided, but the specific plan for improving the fiber would improve the future work. The ultimate goal would be to produce a low-cost carbon composite; this should include an assessment of the fiber with the resin to ensure the translational strength. A high-level cost assessment should be included to verify the main benefit of the project. Also, an effort should be included to evaluate additional opportunities to develop FISIPE or another precursor supplier toward a commercial product.
- There remains a large gap between current fibers (approximately 400 ksi) and the target of 650 ksi. It is not clear whether the plan for future work has the potential to close this gap.

Project strengths:

- ORNL has many years of experience from previous projects in the development of low-cost CF.
- The project has made reasonable progress with measurable success, and it has sufficient funding.
- The project is focused on the key cost driver for compressed hydrogen tanks. The project has a high potential of influencing CF costs in the near term.
- Basing the project on textile manufacturing approaches appears to be an effective way to reduce the cost of CF by taking advantage of commercial processing technology. The partners have the materials expertise (ORNL) and processing know-how (FISIPE) to effectively carry out the proposed research.

Project weaknesses:

- Part of the work to optimize the conversion process and precursor production is not exact science, but instead it simply relies on tedious trial and error.
- While the project was well planned and understood, the critical innovation that would presumably lead to the return on investments was not easy to understand.
- Other avenues to cost reduction include materials substitution and increasing manufacturing rates that were not mentioned in the presentation.
- The project team needs to include specific metrics for developing a high-quality aerospace CF. The team needs to have an update on the cost estimate based on the current assumptions.

Recommendations for additions/deletions to project scope:

- The research team should add a partner or effort in the area of cost estimating. It should also consider including others in the fiber industry beyond FISIPE to ensure that precursor development will have a wider impact rather than simply to SGL Group before the project is complete.
- It would be good to develop a better understanding of the impact on final materials properties of polymer dope filtration as well as other aspects of the spinning process that could reduce the number of large-scale

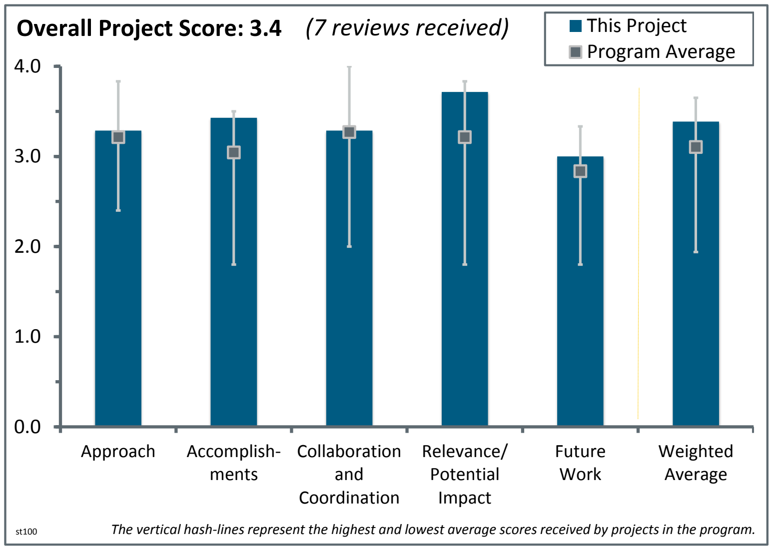
pilot trials. It is unclear if SGL Group plays a role in the project. If so, its role should be described. It has manufacturing expertise that can be brought to bear on this project.

Project # ST-100: Hydrogen Storage Cost Analysis

Brian James; Strategic Analysis, Inc.

Brief Summary of Project:

The objectives of this project are to perform process-based cost analysis of current and future hydrogen storage technologies and to validate the cost analysis methodology so that there is confidence when the methods are applied to novel systems. Sensitivity studies will determine the cost impact of specific components on the overall system. Analysis should identify the most fruitful research paths to cost reduction, including system technology and design parameters, system size and capacity, balance of plant (BOP) components, and materials of construction.



Question 1: Approach to performing the work

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

- The project should add the significant variable of percent yield (both initial production and regeneration) to the sensitivity studies.
- Using Design for Manufacturing and Assembly (DFMA) is a very good approach to identify potential risks and cost factors. The project features a very good overview of 70 MPa system costs.
- The DFMA approach is a robust method for cost estimating for vehicular systems.
- The approach is logical and encompasses the necessary information. The influencing factors are highlighted and appropriately addressed.
- The approach makes sense but the reviewer has no background to evaluate it further.
- Overall, the approach is good because it utilizes DFMA along with industry best practices to develop relevant cost estimates. It is clear that the BOP for the compressed hydrogen tank system is a significant portion of the cost at lower volumes. The approach could be improved by including further cost details on certain BOP components. Also, further cost sensitivity analyses would be useful to highlight the key cost drivers within the tank and BOP, including the effects of certain design assumptions such as pressure and burst factors.
- A clarification on the correlation of vessel length to diameter (L/D) ratio with cost is required. There is a correlation, but costs of BOP dominate at low volumes. The principal investigator (PI) should provide more insight to show why both L/D cost curves are equal. The PI has improved the overall system layout—it is more reflective of a real-world system—and has provided different configurations of L/D, single/multiple setups, etc. This is beneficial to understand the different packaging trade-offs, etc.

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

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

- Progress and refinement of models continue to improve every year.
- The baseline physical assumptions are very reasonable.
- The progress described seems reasonable.

- The project appears to properly address the goals and is focused on achieving the targets in the appropriate time frame. The progress is therefore on a proper time frame.
- The revision of the compressed tank cost estimates provided by this project is important to guide the U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program (the Program).
- The accomplishments and progress with this project were significant since last year's status. The schematic of the compressed hydrogen system was improved, and the cost estimates for this system were better developed at the various volume levels. The project also was able to accomplish and provide results for the regeneration of ammonia borane (AB).
- The project incorporated more up-to-date information from partners of the Hydrogen Storage program, including industry and design and analysis partners. Sensitivity analyses are important in helping to identify future focus areas. The project team should examine the sensitivity to economy-of-scale assumptions such as learning rate(s). Costs for off-board recycling of alane and AB systems may need to be examined as packaged systems rather than one-of-a-kind (typically site-built) systems.

Question 3: Collaboration and coordination with other institutions

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

- All relevant partners for cooperation are included.
- The project team is consulting with the right combination of tank manufacturers, suppliers, and original equipment manufacturers (OEMs).
- The project team has incorporated information from national laboratories, the Hydrogen Storage Engineering Center of Excellence (HSECoE), and a number of industry integrators and suppliers.
- Strategic Analysis, Inc., has a high level of collaboration with others in hydrogen storage research. It has collaborated with the HSECoE and many others in the industry. The analysis coordination with Argonne National Laboratory (ANL) appears to be beneficial for both organizations, while the formal contribution of the National Renewable Energy Laboratory within the project is uncertain.
- The PI is working well with ANL in incorporating ANL's modeling results into cost models. The PI should consider partnering with an engineering, procurement, and construction contractor in the chemical process industry for the project's efforts to estimate off-board regeneration costs of hydrogen carriers. The off-board regeneration work should be reviewed by the delivery and/or production tech teams, where the Program's chemical processing experience resides.
- It appears that collaboration exists, but it is difficult to ascertain the extent of the collaboration. The partners are listed and properly noted. Their areas of expertise are also noted. It would be helpful to determine the extent of the work of each collaborating partner on the pertinent slide where that partner provided information and research.
- More collaboration could be sought.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Accurate, unbiased cost analysis is vital in guiding Program research to maximize the return from research investments.
- This effort provides a consistent basis for cost estimates across the variety of storage development efforts in the Hydrogen Storage program.
- This remains a very important project because there are not many high-pressure storage systems to understand costs available on the market. These systems do not have tremendous deviation in design (as compared to fuel cell engine cost modeling), so results are likely to be more useful and accurate to OEMs. Understanding the cost and potential future savings due to volume and technology improvements will play a critical role in aiding OEMs to make decisions on when/how many hydrogen vehicles to launch in the future.
- This project provides very important information for near-term storage technology (35 and 70 MPa systems) for DOE, OEMs, and suppliers to evaluate their potential business cases. High expected AB off-

board regeneration costs should lead to a higher focus (in other projects) on off-board technology compared to onboard systems.
- The project is highly relevant because it is critically important to have a cost analysis for the various hydrogen storage options. Because it is difficult for researchers to develop cost projections and inappropriate for OEMs to provide their cost estimates, this cost analysis project provides DOE and others with a baseline understanding of the economic potential of the various storage options for both the vehicle cost and fueling cost.
- The approach and layout of the project addresses the relevance of the DOE goals well. The project is developing the appropriate cost analysis to direct DOE efforts and also is effective in determining the directions that need not be pursued. Overall, the project is effective and providing the information needed to support the Program.

Question 5: Proposed future work

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

- The project has a logical path forward in continued support of the Hydrogen Storage program.
- The proposed future work elements seem reasonable, but the reviewer is not an expert in this area.
- This project features good, comprehensive proposed future work packages to predict system costs. The system layout represents the current state of the technology. It is unclear what an advanced system layout could look like and what the impact would be on the BOP costs.
- The scope of the future work looks acceptable, but much of the work is validating previous assumptions and work. The future work needs to be focused on advancing the project, ideally by taking the advancements of associated hydrogen projects to provide ongoing cost impacts and potential improvements. The cost analysis of onboard hydrogen storage meets the requirements of effective future work, but the other items noted do not advance the project and should be improved.
- The project team should provide more detail on why L/D cost curves overlap, as well as itemize some of the BOP components to highlight the fact that they dominate the cost curve.
- The plan for the future work was relatively vague. It could be improved by highlighting the key areas of uncertainty for the compressed hydrogen system and proposing a list of other onboard storage systems to be analyzed based on their potential commercialization from industry interest or previous analysis. For example, a cryo-compressed system may be useful to analyze as the next onboard storage system due to a significant interest from BMW. A further validation step would be useful in the future to compare the model projections to actual tank or BOP costs.

Project strengths:

- The approach and logistics undertaken look to be the strengths of the project. The project organization is also excellent.
- This project is covering a good combination of system configurations. It is useful to OEMs for packaging requirements.
- The experience of the project team, particularly with DFMA for onboard systems, provides a solid basis for consistent estimates across the Hydrogen Storage program.
- This project plays a key role in understanding the impact of cost for the various hydrogen storage systems. Strategic Analysis, Inc., is highly capable and works well with other organizations.

Project weaknesses:

- It is not clear how the barrier “system lifetime assessment” is addressed.
- The future plans or next steps were not clearly defined. Comparisons and validation of the cost analysis projections should be included in order to promote confidence in the values.
- Based on the questions following the presentation, the technical content could be questioned. The questions were pointed toward some assumptions that appeared to not be technically or commercially feasible. Other data, such as carbon fiber pricing, were very conservative and may not completely reflect the current market situation. Consequently, the technical approach and some assumptions could be improved.

- The AB cost analysis did not take into account the impact of handling hydrazine, a toxic, highly flammable compound that requires substantial use of personal protective equipment. Exposure must be monitored and kept below 0.1 ppm. This is not trivial.

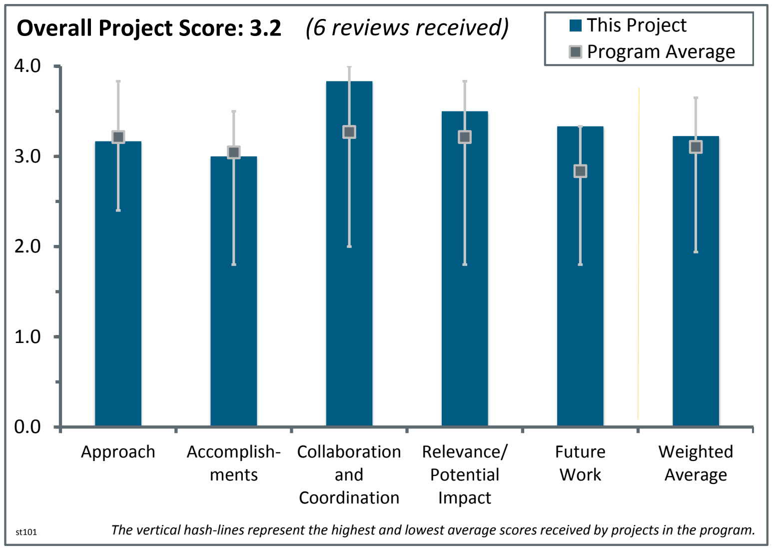
Recommendations for additions/deletions to project scope:

- The input parameter of the cost model should be checked regularly in order to be sure that the assumptions are correct and up to date.
- The hydrazine recharging of the AB cycle probably would make this system uneconomical.
- Cost targets need to be brought to a more current basis year. This is a Program issue that will flow down to the programs and projects. The hydrazine-based AB recycle path, given current hydrazine prices, seems very unlikely to approach the cost targets and should not be pursued further.
- Researchers should accelerate the cost projections of other hydrogen storage systems for comparison to compressed storage systems.
- The project scope could be improved by incorporating the advancements of other hydrogen projects into the costing model. This would in effect allow this project to keep up on technological advancements and not reflect a dated state of the art. Also, industrial partners could be better utilized and provide input for creating such assumptions as labor, production rate, material costs, etc.

Project # ST-101: Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks

Kevin Simmons; Pacific Northwest National Laboratory

Brief Summary of Project:



This project works to improve the individual constituents of hydrogen storage tanks for synergistically enhanced tank performance and cost reduction. Planned project milestones include: (1) developing a baseline cost model for an onboard vehicle capacity tank and comparing cost against prior U.S. Department of Energy (DOE) studies; (2) designing and modeling a new tank with enhanced operating parameters of pressure and temperature for an equivalent tank with alternate fibers and/or a new fiber placement technique and developing a cost model for the new improved tank; (3) developing a feasible pathway to achieve at least a 10% cost reduction for a compressed hydrogen storage tank through detailed cost modeling and specific individual technical approaches; (4) demonstrating integration of modified carbon fibers (CFs) and alternate/modified resins; and (5) conducting a baseline subscale prototype tank and burst test.

Question 1: Approach to performing the work

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

- This project is straightforward work.
- It is a very good approach to create a model, simulate some improvements, and validate these simulations with hardware.
- The project is taking a comprehensive look at many approaches to reduce tank costs and is supported by strong modeling efforts.
- Barriers were clearly addressed and explained in the presentation. The project is well designed, appears to be feasible, and is well integrated with other efforts.
- The work to establish a baseline cost and reduce tank costs and mass through engineered material properties via the efficient use of CF is very good. The main cost drivers are the fibers; nevertheless, the project seems to strongly focus on the resin, where only a limited cost improvement is expected.
- The organization of this project is excellent. The principal investigator (PI) has developed specific tasks for each collaborator and set appropriate goals and follow-up activities. This is the best organized project that this reviewer has had the opportunity to review. The modeling task stands out as a highlight of the project. However, the approach does not adequately address innovative ways to meet the DOE Hydrogen and Fuel Cells Program's (the Program's) aggressive goal of reducing tank costs by 50%. Replacing epoxy resin with vinyl ester (VE) resins is a good step, as is working with a fiber supplier to create a sizing that is compatible with VE resins. By combining these efforts with the fiber type modeling, the project can reach the 10% target milestone for year 1. There exists, by the project's own declaration, a cost savings of 40% still to be realized, but there are no innovative ideas or plans on how to achieve this goal. Simply stating that the remaining savings can be realized by reducing the performance of the tank has merit; however, one would think that if this is then the goal, the overall project is overstated and should be focused on developing the optimized pressure vessel design that shows the most efficiency in capacity, performance, and cost. The model that was developed can greatly assist in this effort. If all pressure vessel projects are aimed at producing a 700 bar tank and it is determined by this project that the ideal tank is

different than the 700 bar design, then an overall directive should be issued to focus on modeling the optimum tank size and performance. The best outcome and value for this project is to determine what the optimum tank design should be for hydrogen storage. Working on optimizing resin, fiber, and wind patterns is something every pressure vessel manufacturer does on a daily basis and may not be providing benefit to the Hydrogen and Fuel Cells Program.

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

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

- The project team has made significant progress.
- The project appears to be making clear progress toward DOE goals. The clarity of the presentation indicates that barriers will be overcome.
- Several potential cost-saving strategies have been identified. "Waterfall" charts showing potential system improvements should be accompanied by credible strategies for achieving targeted improvements or some idea of how likely improvements are. The basis for the improvements should be explained and justified by preliminary experimental accomplishments.
- The work to optimize resin, fiber, and winding efficiency is good and nicely done. The development of the modeling program is also a notable accomplishment and will provide a tool for future work. The milestones for year 1 have been met and should set the basis for future work, but the overall project goals are still very distant.
- The project team developed a feasible pathway to achieve at least a 10% ($1.5/kWh) cost reduction, compared to a 2010 projected high-volume baseline cost of $15/kWh for 350-bar Type 4 pressure vessels, through detailed cost modeling and specific individual technical approaches. The data collected so far is very good, but it has to be validated.
- The predicted cost savings of 10% are good; however, it is not clear how the total cost savings of 37% will be reached.

Question 3: Collaboration and coordination with other institutions

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

- The project is exemplary in terms of the degree to which it interacts with other entities and projects.
- All relevant partners are involved.
- The collaborative effort of each partner appears to be very well coordinated and executed. The PI is doing a nice job of keeping the partners on task and focused.
- This project's active collaborations with Hexagon Lincoln; Ford Motor Company; Toray CFA; and AOC, LLC include round-robin tests.
- The project is utilizing the expertise of fiber, resin, and tank manufacturers and original equipment manufacturers.
- The partners are competent.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This project features a comprehensive approach to bring costs down.
- This project involves reducing pressure vessel cost, mass, and volume.
- A broad study such as this one will advance progress toward the Program goals in terms of understanding the general connection between materials and cost.
- Because compressed tanks appear to be the leading technology for hydrogen storage, accurate modeling of cost and performance is a vital competence for the Program.

- The project's goals and ideals of removing 50% from the cost of the hydrogen storage tank are very aggressive. This project, however, will struggle to meet those goals in its current format. The relevance of this project lies in its development of a modeling technique that can compare cost and performance of a pressure vessel. This model can then have a significant impact on the Program given its appropriate use. The manufacture and testing of pressure vessels are important to validate the model, but they will not provide the necessary impact relative to the high funding level of this project.

Question 5: Proposed future work

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

- This project features a very good approach by validating modeling results with real hardware and tests.
- The validation of predictive models with experimental data is necessary and should be done.
- The team has effectively planned its future in a logical manner and has a clear understanding of DOE barriers.
- The project has a clear path forward aimed at achieving and validating additional incremental advances to lower tank costs.
- The future work of the project as planned does not add value to the overall outcome of the project or allow the project to advance beyond the 10%–15% cost savings already identified. The most valuable aspect of this project will be the ability to utilize its modeling technique to identify the optimized tank geometry and performance level. This modeling effort could provide the necessary input for all storage projects because it either defines a new optimized tank or validates that the 700 bar design is the best for overall capacity and cost. Once the ideal tank geometry and working pressure are identified, the Program can model the most efficient design parameters and fiber arrangements.

Project strengths:

- This project features a good approach and accomplishments.
- If simulations turn out right, this project represents a very good advance in cost reduction.
- The project is very well planned and managed.
- There was a very good visualization of project structure, assignments, and accomplishments (compare slides 6, 7, 8, and 14).
- The project's organization and follow through are impressive. The modeling work is also a strength that has led to an opportunity to further define the project scope.

Project weaknesses:

- So far the project has focused on simulations. Experimental verification is missing, but it is planned for the future.
- Due to the potential impact the material study could have on structural performance, a more involved material study may be warranted, such as testing for an additional weight percent. This could help distribute the performance of the different additives.
- The future work looks to be a weakness because the efforts do not appear to further address the remaining 40% cost reduction goal. The effort to optimize the use of different fiber types is the right approach. However, the future work does not appear to leverage the success of the modeling effort with an optimized pressure vessel geometry and ultimately the efficient use of different fiber types.

Recommendations for additions/deletions to project scope:

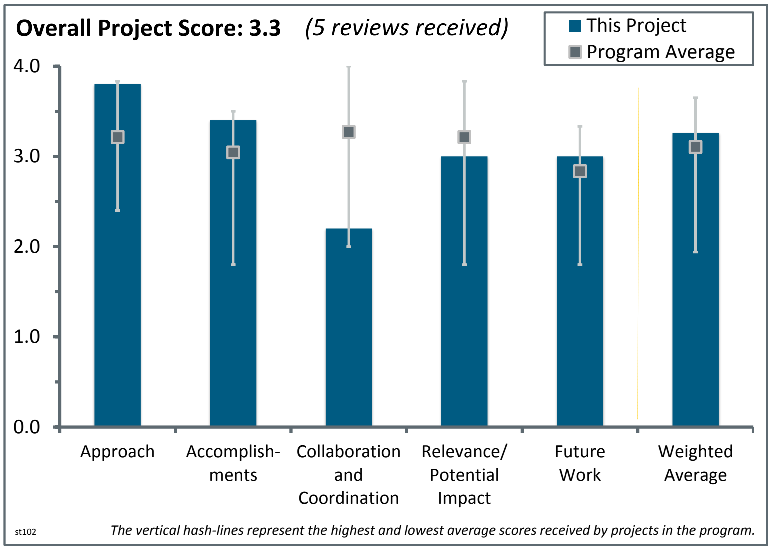
- Funding should be diverted from manufacturing and testing pressure vessels in order to concentrate efforts on determining the optimum pressure vessel size and performance. This recommendation is based on the PI's comment that by reducing the working pressure design to 500 bar, the remaining 40% savings could be realized. If this is the case, then all efforts should be focused on validating this comment so that all other storage projects can be recalibrated to a new, optimized hydrogen storage pressure vessel design. Only then should a tank be manufactured and tested to validate the findings. This new standard could be the biggest

benefit to the overall Hydrogen Storage program because there would be many ways to build this optimized tank using alternative fibers, mixed fiber types, or modified resins, and several manufacturers would be able to commercialize their own cost-effective solutions. Refining the scope of this project to a narrower task could provide an opportunity to reduce the funding to an appropriate level.

Project # ST-102: Room Temperature Hydrogen Storage in Nano-Confined Liquids

John Vajo; HRL Laboratories, LLC

Brief Summary of Project:



The objectives of this project are to: (1) develop hydrogen storage materials that are compatible with the vehicle engineering and delivery infrastructure for compressed gas storage and (2) use measurements and simulations to characterize, understand, and optimize the (enhanced) hydrogen storage capacity of nano-confined liquids (liquids confined within nanoporous scaffolds). The project also works to establish procedures for measuring hydrogen sorption (solubility) in liquids and liquid-based composites at pressures up to approximately 100 bar, validate procedures with bulk solvents, determine the enhanced solubility of nano-confined liquid composites, and develop a simulation scheme to understand the enhanced solubility effect.

Question 1: Approach to performing the work

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

- The principal investigator (PI) has used accurate measurement techniques to measure hydrogen capacities of nano-confined liquids.
- The quality of research is excellent and work has been focused on capacity targets. The PI has carried out careful measurements and has verified these with repetitions and assessment of errors.
- The project is focused on looking at novel sorbents, notably, liquids confined in nanopores, building on a set of papers from the National Center for Scientific Research (CNRS) in France. The experimental work and approach is truly outstanding. The computational work is less so as that is not the researchers' domain of expertise. They should collaborate with an external group for the simulations and not focus on this aspect.
- This project has a great degree of novelty. It may be fruitful with a slightly stronger focus on experimental science and by utilizing theoretical methods to verify the physical measurements.
- The approach to the project is adequate.

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

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

- The researchers have made excellent progress in showing that it is unlikely that this approach will work. They clearly show that the French work is not correct or that it is not the same material with which they are working. They may find a material that works by September 2013, but this will be difficult. However, they have built a unique screening capability that is perfect for testing whether an approach will work or not. This provides a critical testing capability to the DOE Hydrogen and Fuel Cells Program's storage projects.
- Although the research results are opposite to those expected, the presented work explored another interesting idea, which unfortunately did not work out. The project deserves a rating of "good" because negative results are valuable ones.

- Accurate measurements of solubility effects appear to show no enhancement effect. Confirmation that the effect is not real is a valuable contribution to the DOE Hydrogen and Fuel Cells Program (the Program), allowing it to refocus on more promising technologies.
- Good progress has been made on project goals; however, the results and accomplishments do not contribute significantly to DOE goals. The results appear to indicate that the initial reports of enhanced hydrogen solubility in nano-confined liquids are at best grossly exaggerated and at worst false.
- The experimental measurements are challenging and ongoing.

Question 3: Collaboration and coordination with other institutions

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

- The project appears to be well coordinated. The project is based on completely new ideas, and there is little other similar or relevant ongoing work elsewhere, which naturally limits the possibilities for collaborations.
- There is limited collaboration, but this is not a significant weakness for this project.
- There were only a limited number of collaborations; however, in this particular case, an extensive collaboration would not help anyway.
- The work seems to have been done completely at the sponsoring organization, although the PI has reached out to other institutions in discussion. Attempting to obtain a sample of the scaffolds used by CNRS researchers would have addressed the remaining discrepancy between U.S. and French results. A more active collaboration with the CNRS group is recommended.
- It does not appear that the researchers are collaborating as closely with others as they could be. They need to be more closely linked to the French group in terms of materials. It is unclear what material the French group really had. They also need to collaborate closely with a good theoretical/computational group. The current theory work is quite naïve, and they are not using the best potentials for the molecular dynamics simulations. They need to collaborate in the experimental structural work as well to back up their really nice and carefully done work.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This is an extremely interesting and important project based on novel ideas. It is a high-risk/high-gain project. The project will undoubtedly lead to new fundamental science insight.
- The impact could have been quite significant if the idea had worked out.
- Although the results so far are valuable in terms of establishing whether nano-confined liquids are useful storage media, they do suggest that the project will have little impact toward providing storage methodologies that meet DOE targets. If the scaffold without solvent has higher storage, then it is hard to see a path forward.
- The researchers’ work is really excellent, even though they mostly have negative results. The work shows that this technology has real issues and that this can only be demonstrated by careful experimental work. Their go/no-go decision is likely to be a no-go based on their results, but the researchers should continue and explore other options with their very careful and high-quality experimental work. They have built a really nice experimental measurement system and this should be used to explore other options.
- Because the enhanced solubility effect is negligible, the value of additional work in this area is highly questionable.

Question 5: Proposed future work

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

- The project is well organized and has a good research plan.

- Investigating different solvents and scaffolds is the best avenue open to see if this proposed solubility enhancement has any merit. There is less future in the simulations, especially because the PI indicates that he is unlikely to include hydrogen explicitly in these calculations. The project needs a successful result before simulation can be used to (a) verify that the simulation agrees with the experimental result, (b) give some insight into the mechanism of increased solubility, and (c) explore whether other systems offer better performance. Without a robust experiment to compare with, the value of simulations will always be called into question. Therefore, the PI should focus efforts on experiments that could meet the go/no-go decision later in the year.
- The experimental work is very good, but the computational work is not at the same level due to a lack of expertise. The researchers need to focus on being able to treat hydrogen in their MD simulations. Just looking at the vacant space does not provide much information. They need to use better potentials—such as CLAYFF or one of the force fields for silica—and combine these with the force fields for liquids as published by B. Smit and J. I. Siepmann or the force fields of Peter Cummings. They need to model hydrogen in hexane as the test case for their potentials. The CHARMM potential is probably not the best to use because it was developed for biomolecules such as proteins and DNA in aqueous solution, which is not what they are studying.
- The research project should be rethought based on the new results presented at the review meeting.
- Given the fact that the enhancement effect is either non-existent or much less than previously reported, DOE should consider termination of this project.

Project strengths:

- A strength was the highly professional way in which the project was handled.
- This project features excellent experimental methods and quality of research.
- This project features excellent, high-quality experimental work and very careful measurements.
- The project is based on novel ideas; some preliminary investigations have already been conducted.
- This project features careful, accurate measurement capabilities and a strong understanding of hydrogen storage.

Project weaknesses:

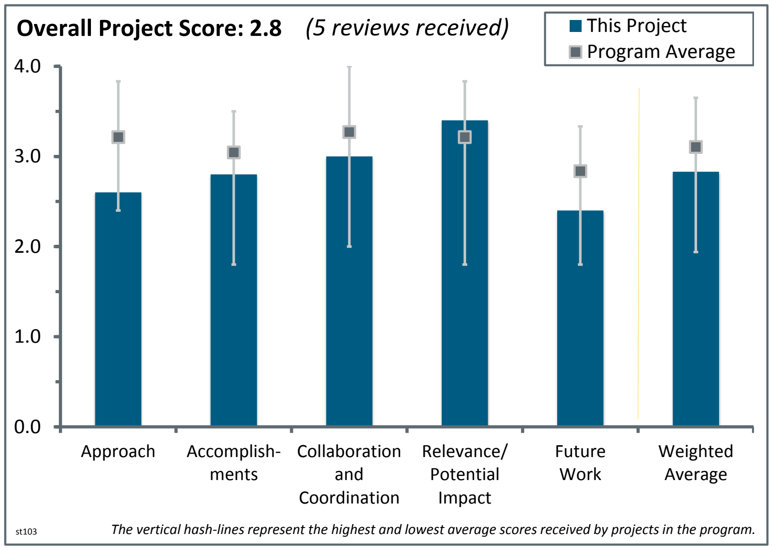
- Stronger preliminary studies should have been conducted before the proposal was submitted.
- Unfortunately, the effect reported by earlier workers cannot be reproduced and may be an experimental error. Engagement with the original group could have been given a higher priority.
- The computational aspects could be stronger. There is an issue with the chosen system based on CNRS reports. It is unlikely that it will work.

Recommendations for additions/deletions to project scope:

- The project should be continued even if the go/no-go is not met in September 2013. The experimental capability should not be lost, because it is very important to the Program.
- It may be fruitful to focus more on experimental measurements and utilize modeling to verify and analyze the observations.
- The researchers should focus on experiment rather than simulation, but even here there is no reason to expect success. The work should be firmly focused on an experimental demonstration to set the go/no-go decision. The relatively low storage capacity measured is unfortunate because the PI has undertaken some excellent experiments and has developed valuable expertise for careful measurements of this type.
- The project should be closed, based on the progress results obtained to date.
- The project should probably be terminated at the September 2013 go/no-go point if no compelling evidence is observed for nano-confined enhancement.

Project # ST-103: Hydrogen Storage in Metal-Organic Frameworks

Jeffrey Long; Lawrence Berkeley National Laboratory



Brief Summary of Project:

The objectives of this project are to: (1) research and develop onboard hydrogen storage systems that allow for a driving range of greater than 300 miles, (2) identify materials with the potential to meet the U.S. Department of Energy (DOE) mass and volumetric capacity targets for reversible uptake, and (3) synthesize new metal-organic frameworks (MOFs) capable of achieving the adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures.

Question 1: Approach to performing the work

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

- This project uses a combined synthesis, modeling, structural characterization, and hydrogen uptake measurement approach to develop new MOFs that will meet DOE objectives. The project team has the highest qualifications for achieving these goals. The modeling and characterization strategy for optimizing the search for the most promising MOFs is a good approach that will hopefully prove successful.
- This is a high-risk, high-reward project geared toward the synthesis and characterization of MOFs that have highly exposed metal cations that can, in theory, provide active sites for multiple hydrogen binding. This may increase the gravimetric capacity and operating temperature of sorption-based hydrogen storage systems; however, the recourse to higher-surface-area materials with larger pore sizes and extra volume to accommodate analogous ligands than can support the metal cation may lead to lower packing density and thus, lower volumetric density, which is already short of meeting DOE targets. The project should clearly show the advantages and disadvantages of the approach.
- This project has a rather DOE Basic Energy Sciences (BES)-program-level approach and tends toward addressing fundamental issues. Thus, its impact on obtaining the DOE Office of Energy Efficiency and Renewable Energy hydrogen storage goals suffers. The approach from a fundamental science perspective is good, but it may not have a substantial impact on overcoming the mass and volumetric barriers that the chosen materials class faces.
- The group is very good at making and characterizing MOFs. However, a convincing path for improving the enthalpy of adsorption was not provided. It appears that the team is pursuing several approaches without an overarching strategy in mind. Importantly, General Motors' work scope seems to be at odds with the major goals of the project. For example, slide 3 of the presentation states that one goal is to develop MOFs that will work at pressures below 100 bar. It is therefore unclear why the effort is devoted to developing a pressure, concentration, and temperature system that can measure uptake at pressures up to 350 bar. The Hydrogen Storage Engineering Center of Excellence (HSECoE) has shown that at pressures above approximately 200 bar (the "crossover pressure"), physical storage outperforms storage in MOF-5. It is unclear why these high-pressure capabilities are needed. This component of the project should be discontinued unless a clear rationale for its existence can be provided.
- The general approach seems good, with an appropriate balance of empirical and computational effort in developing sorbent materials for hydrogen storage. However, the need for Task 4, development of a high-pressure hydrogen adsorption measurement to 350 bar, is unclear. Previous studies have shown that the benefits of using a sorbent material occur below 200 bar, so a high-pressure measurement device beyond 200 bar is not necessary. The project should focus on demonstrating the feasibility of multiple hydrogens at

a single binding site, which should be further clarified in the approach. Also, the isosteric heat should be consistent throughout the adsorption curve, rather than accepting significant variations.

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

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

- Considerable technical accomplishments have been achieved in a short period of time, and most of the milestones have been met. New MOFs should be tested for hydrogen uptake as they are produced, even if at lower pressures than 350 bar; this will be a good predictor of capacity and enthalpy values.
- The project demonstrated the ability to prepare functionality ligands, allowing for post-synthetic insertion of metal cations, and prepared two new MOFs containing coordinatively unsaturated high-valent cations. However, the results of cobalt and nickel analogues show that the higher hydrogen binding enthalpy only exists at low coverage (less than 1 wt.%) and drops sharply to its normal value at higher coverage; therefore, it is presently more of a penalty than an advantage.
- Scientific progress has been very good; however, progress toward overcoming the mass and volume barriers is coming along at a much reduced rate. The progress has been hindered by not having access to adequate, high-pressure measurement systems from the beginning of the project. This task is now only 30% complete, one year into a potentially three-year project.
- The accomplishments were outlined in the presentation, but it was difficult to evaluate if the completed tasks were making enough progress toward the objectives. The isosteric heat curves indicate the potential improvement in binding at the metal sites at low pressure before transitioning to traditional surface adsorption. This characteristic actually could be a negative characteristic because the sorbent material would benefit from having low binding energy at low pressures to maximize capacity.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration between the materials side and the neutron scattering effort is clearly going well.
- This project has a very well qualified group of researchers that have demonstrated that they communicate and work together as a productive team.
- The coordination between the project partners seems to be effective. The project could benefit from connecting directly with the effort on adsorbents within the HSECoE to develop a system perspective on the material targets and needs.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The project is highly relevant to the overall DOE Hydrogen and Fuel Cells Program objectives.
- The higher operating temperature of physisorption-based storage will significantly advance progress toward DOE goals.
- This project could have a significant impact if it is able to increase the enthalpy of sorbent materials used as hydrogen storage materials operating at ambient temperatures.
- This project could, in principle, align with DOE RD&D objectives in hydrogen storage. However, the relevance of this project suffers due to the rather BES-like approach. While this results in very good science, the focus on advancing the state of knowledge to address the volume and weight barriers in the applied-research oriented Hydrogen Storage program falls short and limits the potential impact.

Question 5: Proposed future work

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

- The future work appears to have a focused plan. It would be helpful to identify the key steps that could potentially close the significant gap between the current status and the target.
- The volumetric storage capacity is as important as gravimetric, if not more, given the present drawbacks of compressed hydrogen storage. The project should concentrate on improving both, and not one at the expense of the other.
- The in silico screening technique seems very promising. There should be enough data on currently known MOFs to validate the concept. It was a little surprising that more validation of this search method was not presented in this year’s work; it should be given a high priority with a go/no-go decision.
- Not many details were provided regarding future plans. It is unclear exactly how computation will be used to guide experiments. Thus far, computation has operated as a reactionary mechanism by calculating enthalpies of known compounds. It is unclear if and how predictive calculations will be performed.
- The proposed future work does not provide a well-designed pathway to address the weight and volume barriers the team has subscribed to toppling. The future plans could be improved by discussing, for example, the potential to improve the hydrogen absorption energies well beyond a few moles per gram of material, or a realistic plan for achieving far more than one mole of hydrogen/metal site in order to provide some relevant pathways to addressing the mass/volume barriers in a meaningful way.

Project strengths:

- The project features a good mix of capabilities and expertise for materials synthesis.
- This project features a team that is very good at approaching scientific problems.
- This project features a strong, very knowledgeable team.
- The project has both empirical and computational aspects to the project, which provides a strong validation aspect to the project.
- This project has a well-organized team with clear goals and the potential to meet DOE targets. Work has progressed rapidly, with a number of results to show in the first year. However, more hydrogen uptake and enthalpy data would have been expected at this point. The future work is in line with the strong progress of this project.

Project weaknesses:

- This project lacks an overall view of material-based hydrogen storage system requirements.
- More hydrogen uptake and enthalpy data would have been expected at this point.
- The overall direction/strategy is hard to see. The high-pressure measurements seem unnecessary.
- The project should confirm alignment with the system requirements. The project should avoid the development of high-pressure measurement equipment.
- Weaknesses include the lack of high-pressure adsorption characterization capability and the lack of a well-posed roadmap to address the volume/weight barriers in the remaining two years of the project.

Recommendations for additions/deletions to project scope:

- The in silico screening technique should be validated using the multitude of current data available, and hydrogen uptake measurements should progress rapidly.
- Once the researchers have an operable calibrated adsorption system, providing both adsorption and desorption data to demonstrate cyclic capacity would be most interesting to determine if the “20kJ/mole fraction” of hydrogen bound to the metal center upon adsorption of hydrogen is released upon pressure letdown under realistic adsorption system temperature ranges. This should be a requirement for all of the projects that are attempting to improve the capacity of adsorption systems by this pathway.
- It is unclear why there was so much effort to go to 350 bar with the characterization when the project objectives include achieving storage under 100 bar. The additional characterization of the volumetric capacity and the reversibility of the synthesized materials would definitely help the project.

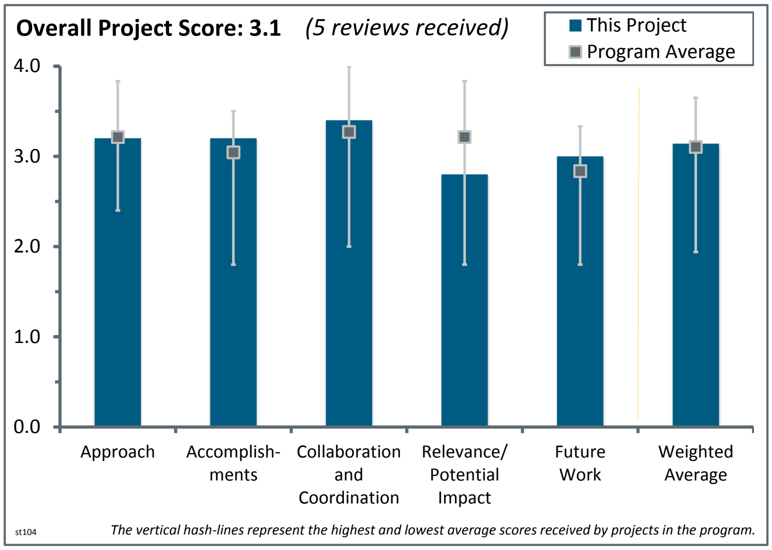
- The research team should delete the high-pressure measurements.
- The researchers should delete the effort associated with the high-pressure isotherms or confirm that an adsorption system would still provide a benefit in comparison to a high-pressure compressed system.

Project # ST-104: Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing Hydrogen Storage Materials

Shih-Yuan Liu; University of Oregon

Brief Summary of Project:

The objective of this project is to develop novel chemical hydrogen storage materials that have the potential to enable non-automotive applications and vehicular applications. The focus of the material development efforts is on compounds that maintain a liquid state while demonstrating reversibility and reasonable kinetics at moderate temperatures. Tasks in this project will address synthesis of proposed materials, characterization and scale-up of the synthesized materials, and fuel cell testing.



Question 1: Approach to performing the work

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

- It is an interesting approach to attempt to meet sorption metrics with heterocyclic materials of variable structures and physiochemical properties.
- The University of Oregon is leading an integrated project to discover and characterize compounds with the potential to serve as liquid-phase hydrogen storage media. This approach is most appealing because it focuses on providing reactant and product species that can be handled throughout the hydrogen storage process as liquids to facilitate filling and discharging the fuel. The project includes an excellent combination of complementary capabilities that range from the work at the University of Alabama, which utilizes first-principles theory to identify viable candidates from both model thermodynamics and predicted reaction pathways, to the University of Oregon's innovative synthesis methods to synthesize the candidates. The project also characterizes key chemical and physical properties of original compounds and products following hydrogen desorption. The involvement of a fuel cell company to assess the performance of the more promising compounds is very useful in order to identify detrimental issues before committing time and resources to doomed materials.
- The initial approach to this project was excellent. An inspiration based on chemical intuition was backed by a first-rate computational study, which was followed by highly skilled synthesis and characterization of novel compounds. The more recent studies seem to be drifting away from the original goal of developing a hydrogen storage material that can meet the U.S. Department of Energy (DOE) H_2 Storage Light-Duty Vehicle (LDV) targets, but they could be applicable to the DOE H_2 Storage Portable Power targets.
- The project is well defined and contributes to overcoming some barriers. There is clear coordination between computational efforts and experimental synthesis. The project is nicely focused on three classes of compound liquids (in both states), as well as potentially reversible and high-capacity exothermic systems. However, the liquids and reversible systems are likely the most useful. The idea to use Compound B or other liquids as a carrier liquid for ammonia borane (AB) is a great idea and should be considered for other slurry systems (such as AlH_3 and $LiAlH_4$) if there are no compatibility issues. The purpose of the polymer electrolyte membrane fuel cell demonstration is unclear. Running a fuel cell for 30 minutes does not really prove anything—it may be better to focus on the mass spectrometry of the released gas to determine impurities.
- The approach to onboard hydrogen storage using recyclable, liquid carriers provides opportunities for the engineering of onboard systems. While many of these "prototype" liquid carriers cannot meet current

gravimetric capacities, they provide an excellent platform for demonstrating the proof of principle of onboard storage systems. The team has demonstrated that hydrogen release from these CBN compounds can occur catalytically and that the catalyst may be a heterogeneous catalyst—a feature that is important both to an engineered hydrogen release reactor and to the contribution to the ease of separation of catalyst prior to regeneration. The approach the team takes is rational. The team aims to take advantage of the propensity of boron-nitrogen-containing compounds to rapidly dehydrogenate, and then to down-select to compounds that remain in the liquid state over the relevant range of conditions in both hydrogenated and dehydrogenated forms. The approach the team takes to develop potentially reversible systems by choosing the thermodynamically middle ground is a good first-order approach, but there is more to reversibility than cataloging compounds that have a delta-G of around zero. The team should better define the meaning of a more detailed analysis of the thermodynamics of practical reversibility. This would be useful guidance for current and any future liquid carrier projects. The approach of using the liquid carrier as a “solvent” for a higher capacity material is a good one, but this approach needs to also incorporate the additional complexity of regenerating an even more complex mixture.

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

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

- This project has made excellent progress over the past year. Although there seem to be no clear winners yet, a number of interesting new compounds have been proposed and synthesized. Even if the reversible capacities of these materials remain low, they could be extremely useful as carrier liquids (although this may complicate regeneration somewhat). Experiments with Compound B and AB look especially promising because the spent fuel remains liquid even at room temperature. The isolation and characterization of intermediates that form during decomposition have shown nice progress.
- Much has been accomplished toward several, perhaps not all, of the barriers the team has chosen to address. Good progress has been made in the areas of compound synthesis and characterization. Good initial progress has been shown in providing proof-of-principle fuel cell testing, albeit for a very short time (it is assumed that materials limitations/costs are an impediment here). As usual, the theory component at the University of Alabama has been very productive and focused on the problem at hand—suggesting potential reaction pathways for hydrogen release from these molecular CBN compounds. It speaks to developing a more advanced knowledge of structure-function relationships in this class of hydrogen release compounds.
- Excellent progress has been made toward completing the proposed tasks. The majority of the target compounds have been prepared and characterized, and their dehydrogenation behaviors have been elucidated. A number of insightful mechanistic studies have also been carried out. Unfortunately, the work does not seem to be progressing toward the development of a material that will meet DOE’s targets.
- So far during this project, 9 of the 12 proposed candidates were prepared and at least partially characterized. However, only one (i.e., Compound B, shown on slide 9) appears to be a liquid-state hydrogen carrier and its likely hydrogen storage capacity is only 4.7 wt.%, which is below the 2012 DOE gravimetric target. Substantial characterizations of the relevant chemical and physical properties of Compound B were done at Pacific Northwest National Laboratory. Protonex also tested this material as a hydrogen source to operate a fuel cell. There are numerous issues with various properties, including thermal stability, reverse hydrogen recharging, and impurities in the released hydrogen gas that need further investigation. It is not clear whether these shortfalls can be overcome to provide a practical storage candidate that can satisfy the DOE targets for vehicle or other applications.
- The researchers found a very limited number of materials that had the physiochemical properties needed. However, they did conduct a thorough investigation. The principal investigator (PI) was not aware of the need to retest fuel cells after exposure to hydrogen stored in their materials. The impurities may greatly reduce the longevity of the cells, but a limited test is not adequate.

Question 3: Collaboration and coordination with other institutions

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

- This project features excellent coordination with the theory partner and close, appropriate collaboration with other institutions.
- There appears to be excellent interaction among all four major partners involved in this project. Their activities are very complementary and appear to be highly coordinated. The work seems to be a model of cooperation for other teams to follow.
- The team continues to operate in a very collaborative, open format. The project continues to incorporate input on engineering-related issues such as viscosity, impurities, etc., and thus demonstrates good communication with the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- There is good collaboration and coordination within the project team but no outside collaboration.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.8** for its relevance/potential impact.

- This is one of only a few projects with the potential to significantly advance progress toward DOE RD&D goals and objectives. Similar to other projects of this type (focused on materials discovery), progress often seems slow because no new capacity records have been set. However, this is one of the more promising areas for hydrogen storage at the moment and this is an excellent team.
- The utility of liquid hydrogen carriers in addressing vexing engineering problems in onboard hydrogen storage systems has been well discussed. This project is relevant to providing proof of principle to addressing the utility of a liquid system that can be readily off-boarded for regeneration. The work this project does is relevant to all of the DOE technical barriers the PI has chosen to address, and there are several. The potential impact of the project suffers somewhat because of the rather low available hydrogen capacity, but the project has demonstrated catalytic hydrogen release capacities and kinetics that are more than competitive with other hydrocarbon-based systems. Their impact could improve if the team can demonstrate hydrogen release from the carbon backbone of these compounds, which would result in improved hydrogen capacity.
- The project is generally relevant in the sense that it explores a highly novel class of compounds that expands the horizon of potential hydrogen storage materials and represents the kind of original thinking that will be required to develop materials that meet the DOE targets. However, the dehydrogenation thermodynamics of these compounds prohibit their direct re-hydrogenation. Suitable physical properties are found only with derivatives with unsuitably low hydrogen densities; therefore, the class of compounds appears to be irrelevant to the DOE H_2 Storage LDV targets.
- The problems lie in the level of impurities and the extensive degradation of the materials.
- The team members appear quite aware of the properties and behavior required from both the reactant and products species in order for these hydrogen candidates to be acceptable for hydrogen storage. They should continue to look at all of the issues associated with producing and handling these materials, including hazard and toxicity potentials.

Question 5: Proposed future work

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

- All of the planned future tasks shown on slide 31 are reasonable and consistent with the objectives of both the project and DOE performance targets. Completion of the efforts needed for the assumed go/no-go assessment at the end of Phase I should be emphasized, including the attempt to prepare Compound E and obtaining more thorough assessments of any other promising candidates.
- The plans clearly build on past progress and are sharply focused on barriers. Compounds E and F look somewhat promising, but full hydrogen removal is needed to access full capacity. It is worthwhile to continue investigations of liquid CBNs as independent storage systems and as carrier liquids with other

high-capacity hydrides (e.g., AB, AlH_3, $LiAlH_4$). The researchers may want to postpone the fuel cell studies and focus on investigating gas analysis.
- The strength of the PI is in the synthesis of new compounds, the catalysis of hydrogen release, and the regeneration of “spent” fuel, and the future plans largely take advantage of these strengths to continue to address the chosen technical barriers. The project team should either consider (a) the complexity of regeneration of “fuel blends” prior to expending effort in fuel cell testing of blends or (b) what the stationary or portable power requirements are to determine if the fuel blends approach makes sense for a “once-through” approach where maybe regeneration is not the main issue. The researchers should continue to improve the communication of this project with the HSECoE.
- The future plans are not directed toward the development of derivatives that will meet DOE H_2 Storage LDV targets.

Project strengths:

- This project is innovative.
- The project is exploring a highly novel class of compounds that expands the horizon of potential hydrogen storage materials.
- There is a good distribution of strong capabilities, as well as collaboration. In general, the plans to move forward are well thought out.
- This is an excellent combination of expertise and capability among the four partner organizations, spanning complementary disciplines. It is good that the researchers are looking at the behavior of Compound B as it supplies hydrogen gas to operate a fuel cell. Similar and longer term evaluations of fuel cell operation are suggested. The past assessments and characterization of AB and related chemical storage compounds are clearly evident in the approaches used with these materials.
- There is excellent coordination between computational and experimental efforts. This type of project can move quickly, using theory to guide the synthesis and materials discovery and further computational efforts to help identify intermediates and reaction pathways. CBN-H materials show good promise, especially the liquids.

Project weaknesses:

- There are a limited number of materials that meet the physiochemical metrics that are needed to be considered viable. No reversible behavior has been reported yet. There is a lack of longer term testing in fuel cell systems.
- The fuel cell demonstration seems like a distraction because it is not really a good test of impurities or impact on fuel cell performance.
- The limited hydrogen storage capacities of nearly all of the candidates remain a major issue with this approach. More information on the stabilities and reversibility of these compounds is needed. The limited ability of the reactant and or product species to remain in liquid phase or solution at temperatures below 300–350 K could be in doubt. Preparation of sufficiently large batches of well-characterized material should be a concern, along with the quantity and composition of impurities released during formation of the hydrogen gas. Finally, the development of effective catalysts for both decomposition and reformation of the storage materials could be a major challenge.
- The project is narrowly focused on a prohibitively expensive family of compounds with the same structural core. Unfortunately, no derivative has been found or seems likely to be found that has the right combination of physical properties, dehydrogenation thermodynamics, and gravimetric hydrogen density to meet DOE targets.

Recommendations for additions/deletions to project scope:

- The project focus should be redirected toward the development of a compound that will meet the DOE H_2 Storage LDV targets.
- The project team should carefully examine the fuel blends issue with respect to regeneration if the main focus going forward is vehicular application.

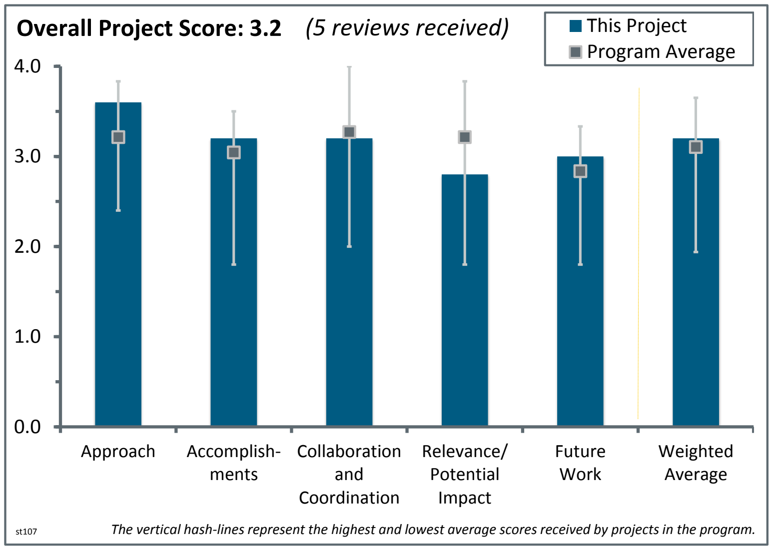
- The scope of tasks and planned activities is sound at this time (for completing Phase I and transitioning into Phase II). The team should devote more time to searching for and identifying impurities released during the hydrogen desorption under conditions needed to operate fuel cells, as well as looking at intrinsic degradation and thermal stability.

Project # ST-107: The Quantum Effects of Pore Structure on Hydrogen Adsorption

Raina Olsen; Oak Ridge National Laboratory

Brief Summary of Project:

The objective of this project is to understand volumetric and gravimetric storage and hydrogen adsorption in a carbon adsorbent with volumetric storage larger than similar carbons, despite having smaller surface area. The research approach includes experimental study of carbon with high volumetric storage, neutron measurements of quantum states of adsorbed hydrogen, and theoretical calculations of quantum states and quantum adsorption effects.



Question 1: Approach to performing the work

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

- The approach to interrogate the carbon adsorbent HS;0B appears to be sound.
- The approach demonstrates a good handle on the use of some theory in conjunction with neutron scattering to attempt to develop a working model of what may be an unusual adsorption site on a particular carbon sample.
- Inelastic neutron scattering is used for measurement of quantum states of hydrogen molecules while they are adsorbed on carbon samples. Computational work is performed in order to understand quantum states and propose a quantum model of adsorption. This is an interesting plan, which may lead to new fundamental science insight.
- This project seeks to explore the phenomenon of excess hydrogen absorption in activated carbons at low temperatures. Experimental evidence for the effect is presented, and a model based on the formation of a Bose-Einstein condensate (BEC) is advanced. Proving the existence of a BEC is no mean feat: preliminary evidence from neutron diffraction experiments is consistent with the phenomenon but key experiments remain to be conducted.
- The approach is generally sound and is directed toward important barriers in hydrogen storage capacity. The link between experiment and theory could be improved. A new BEC has been proposed that could help address the DOE goals, but the experimental evidence to support the existence of this BEC is somewhat tenuous. The inelastic neutron results show some features that are consistent with the proposed structures, but not fully convincing. The principal investigator (PI) noted that more and better DINS data are needed, for example. The proposed pores arising from defects between graphite layers are also somewhat speculative at this stage. It is understood that the flake morphology of the sample naturally aligns graphene layers perpendicular to the TEM viewing direction; nevertheless, the team did not find any of the proposed pores among the observable graphene sheets. It would also be possible (but admittedly more difficult) to prepare TEM specimens looking along the plane of the flakes by cross-sectioning specimens mounted in epoxy, for example, and/or by using FIB/SEM to cut out sections from flakes. In the long term, it would seem necessary to correlate the concentration of slit pores with observed INS features and increased adsorption if the theory is to have merit in addressing storage barriers.

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

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

- Data has been measured and the analysis is in progress.
- The project is making good progress in identifying and characterizing BECs in an unusual hydrogen sorption site. The combination of sorption, Raman, neutrons, and microscopy appears to be well integrated and well thought out. The project addresses the very difficult problem of finding "the needle in a haystack" in these complex, highly heterogeneous materials.
- This is a technically challenging project for which there exist only a limited number of available techniques to explore the unusual behavior of hydrogen in the pores of the activated carbon. Significant progress has been made in characterizing the structural features of the carbon and with the neutron scattering experiments performed to date.
- The HS;0B sample was characterized by a multitude of techniques. Data was not seen in the slides on how many samples/batches were evaluated, but perhaps there was a comment on this during the talk. The researcher seemed well versed in all of the applied characterization techniques and their limitations.
- This is difficult to assess for this project, which is mostly concerned with quantum states in adsorbents and how these might lead to progress toward DOE goals. The accomplishments are in establishing a theory, and the experimental measurements presented are in support of this. The approach is in line with the stated objective of understanding the unusually high capacity of a particular carbon adsorbent. With this approach, progress shows no improvement in the DOE performance indicators (in this case, gravimetric and volumetric storage capacity). However, this does not seem to be the objective of the project, and capacity could improve in the long term as a result of the understanding obtained in the current project. Given the length of time remaining, however, it is unlikely that any improvement in the demonstrated storage capacity will result.

Question 3: Collaboration and coordination with other institutions

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

- There is a strong network of collaborators compared to the small size of the project.
- Good collaborations have been formed within Oak Ridge National Laboratory (ORNL) and experience has been gained for postdoctoral research.
- Appropriate collaborations have been established with other researchers at ORNL and with the University of Missouri - Columbia.
- This project features good collaborative efforts with other ORNL groups, the PI's graduate university, and Buffalo. These bring a wide range of different synthetic, analytical, and computational tools; however, some are a little cursory. X-ray diffraction of primarily amorphous materials is not especially illuminating unless a full Pair Distribution Function analysis is undertaken. The small Raman probe could be used to map the different features in the sample and give some quantitative idea of the heterogeneity. However, the real heterogeneity is likely on a finer scale than the Raman laser and the results obtained may relate to the physical orientation of flakes because Raman signals are sensitive to the relationship between bond direction and laser polarization.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.8** for its relevance/potential impact.

- This is a highly relevant project, seen from a fundamental science point of view.
- The project is clearly relevant to DOE goals. Understanding physisorption, especially new mechanisms, is an important route for developing new materials with improved properties.
- This project is longer term and more speculative in its objectives than most of the others presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review; but, if successful, it would represent a

paradigm change in the approach to hydrogen storage and the capabilities of carbon-based (and other) porous materials. So, although it is not critical to the current activities in the Hydrogen Storage Engineering Center of Excellence, if successful, it would supplant much of the current work in this area.
- In principle, better understanding of the local structure that gives rise to the unusual adsorption phenomenon in the carbon materials studies can lead to new ideas in sorption studies that could be of potential relevance to improved overall gas sorption in solids.
- Slide 3 indicates a maximum of 4.39 wt.% stored hydrogen at 300 K. Although larger than MSC-30, this material clearly will not meet the near-term (2017) material target of approximately 11%. The characteristics of the HS;0B material are curious; they would make an excellent DOE Basic Energy Sciences project, but they do not have the potential to meet the DOE targets. A better understanding of this material, and the underlying phenomena, may allow a future material to be engineered.

Question 5: Proposed future work

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

- This project features a good research plan.
- The proposed future work is sound and builds on progress to date. A hydrogen deuteride (HD) experiment should be conducted as a priority.
- The additional neutron scattering experiments planned will be very valuable in verifying the proposed quantum mechanism because the current results are consistent but not completely convincing. If the results are positive, then further experimental effort should be directed toward identifying the relevant features in the sample.
- The proposed graphene oxide frameworks may be a better way to verify the effect. The inter sheet spacing of these structures appears to be in the <1 nm range proposed and highly regular, judging from the diffraction peaks. These would therefore present a much larger and controlled area that relates more strongly to the theoretical systems studied.
- It is unclear what potential impact the impurities (rust, NaCl) might have on this material. It is unclear if it is possible to make this material in an inert atmosphere, using an acid-cleaned steel container, so as to avoid the “chunks of stainless steel” mentioned on slide 7. Phil Parilla mentioned that the most common impurity in hydrogen sources is H_2O, due to a possible reaction with rust in the tank and subsequent reduction. Additional experimentation to evaluate the impact of water on the carbon performance seems warranted (and a subsequent reevaluation of the synthetic method).
- While the project is ending, the final activities described are good. Examining other “new” carbons for this effect is rational; also, it would be of interest to perhaps look at additional batches of HS;0B to examine whether there is a batch-to-batch reproducibility, particularly because there was apparently a good amount of iron oxides observed. Perhaps this could be related to or associated with the “unusual” porosity.

Project strengths:

- This project features a good combination of experimental and theoretical work.
- This project features an original and ambitious approach.
- This project features good integration of many skills, particularly for a postdoctoral project.
- This project features good productivity, a high degree of novelty, and the possibility of impacting DOE goals.

Project weaknesses:

- The experimental work is difficult and requires specialist facilities (this cannot be avoided).
- At present, much of the work is speculative or supported by experimental data that does not have an unambiguous or definitive interpretation.
- It is unclear how the hypothetical wt. % of stored hydrogen on slide 3 was calculated. In the future, the researchers should annotate the technical backup slides (especially slide 21) so the reviewers can be more quickly calibrated to the spectroscopies used.

Recommendations for additions/deletions to project scope:

- Measurement of the performance of HD under similar conditions is highly recommended. HD is a fermion and will not exhibit a BEC. This experiment could deliver definitive proof of the nature of the observed phenomena.

Project # ST-108: Metallation of Metal-Organic Frameworks: En Route to Ambient Temperature Storage of Molecular Hydrogen

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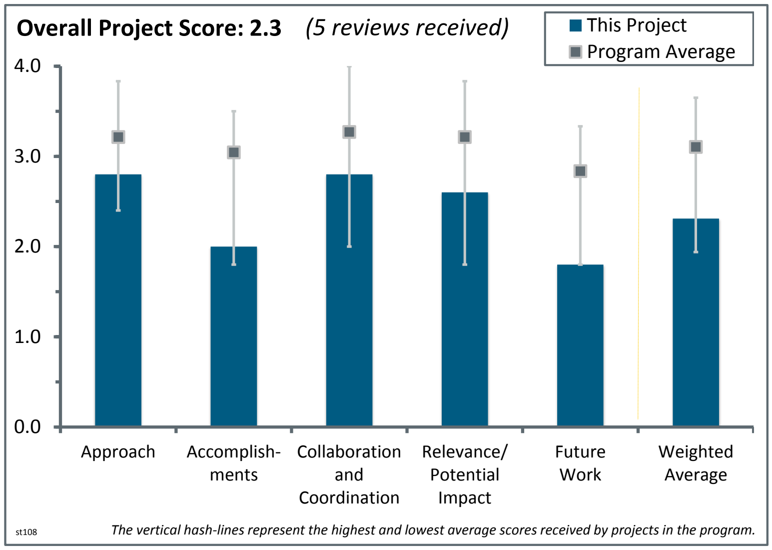
Brief Summary of Project:

The objectives of this project are to: (1) develop functionalized sorbents for metallation, (2) deposit metal ions by solution and atomic layer deposition, and (3) characterize materials and performance. The project adopts an iterative computational and experimental approach to depositing coordinatively unsaturated metal ions on functionalized sorbents.



Question 1: Approach to performing the work

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

- This project has a combined experimental and theoretical approach, which is good.
- The project represents a good exploratory approach to improving sorption properties. The approach is rationally based and extends the work from prior observations that metal ions on frameworks interact with dihydrogen, increasing the sorption energy. The approach involved using several materials platforms to search for evidence of enhanced quantities and energies of sorbed hydrogen on modified materials. It would be valuable and instructive to carry out desorption experiments on such metal modified materials to ascertain whether or not the hydrogen bound at higher energies is desorbed under the "usual" conditions.
- The project has followed sound ideas to improving the storage capacity of metal-organic frameworks (MOFs) by attempting to add additional metal sites for hydrogen adsorption. There are other U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program (Program) projects that are exploring similar avenues. The barriers listed on slide 2 are project goals rather than Program-defined barriers. The investigators should use the Program barriers in the future to show how they are focused on DOE objectives, as suggested on slide 3, where reference to gravimetric and volumetric targets is made. The iterative experimental/computational approach has been overstated. Two slides were dedicated to this. Such an approach is fairly common and may be worth mentioning, but the investigators should focus more on the real approach and accomplishments. Aside from the Q_{st} figures on slide 8, there is little evidence of an iterative experimental/computational approach anyway.
- The experimental/computational synergy is a common approach. The reference article does expound on the method, but it only describes the synthesis of a single MOF to "validate" the method, and the resulting MOF did not perform substantially better than an already known MOF of similar structure (the authors claim the competing MOF has higher methane coordination than their model predicted—additional evidence that the model is poor). Nearly half of the slides are on the approach. Because the project is close to the end, a more concise overview (even though a presentation or poster from last year could not be found) was expected. The project team should convert its gravimetric densities into weight percent of hydrogen in the future. It is very difficult to gauge progress (or potential progress) when everyone uses a different unit in each talk. Also, a percentage excess of the target is a preferred value rather than absolute value.
- This is a postdoctoral research grant to examine the metallization of MOFs. It is clear that there is a very nice balance of autonomy for the postdoctoral researcher to lead the work and guidance/supervision from the mentors, Dr. Joseph Hupp and Dr. Omar Farha. The investigator tried two approaches to metallization of MOFs (i.e., atomic later deposition and solution deposition). The result was that the metallization (or metallation) of the MOF PAF-1 by both approaches led to a decrease in surface area and has not resulted in

achieving the goal of unsaturated metal sites on the MOFs. However, the MIL-101 MOF was able to be metallated without significant loss in surface area. Other issues arose surrounding the loss in crystallinity in the MOF and the limited increase in the enthalpy of adsorption. This increase in adsorption enthalpy was predicted to occur computationally for Zn_2+ and Mg_2+ metallation. With further research, it is possible to overcome these barriers in the MIL-101 system.

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

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

- The project made good progress, and the postdoctoral student gained great value in carrying out this work and forming collaborations to study and characterize the complex materials he was working with. While many of the results were negative results, this exploratory approach is valuable in setting out what can work and what may not work in future approaches to using highly metallated open framework materials as gas sorbents. Progress was made in demonstrating that small aperture materials present problems when involving molecular chemical approaches to the metallation of ligand sites within the void volume. In at least one system, improvements were made in enhancing the energy of hydrogen binding to (presumably) metal sites, with binding energies demonstrated up to 7 kJ/mol and with up to 2 mmol of hydrogen being bound with higher energy than the unmodified framework material.
- The researchers should include a single bullet point at the bottom of each slide indicating the take-home message. It is easier to evaluate progress this way, even for reviewers who attended the session. On slide 12, the researchers should annotate the plots. It is unclear if one data series represented a control. It is unclear if slide 14 is really an accomplishment or if it is an advertisement. If intellectual property issues prevent the researchers from sharing sufficient information to show progress, they should exclude these slides in the future.
- The research encountered a major and seemingly unexpected barrier in the difficulty of metallation (due to small pore sizes). Pore clogging is likely occurring for both techniques. Although progress has been slow, the decision to move to a different MOF (i.e., from PAF-1 to MIL-101) was a good one. The -NH_2 and -OH functionalized MIL-101 remained porous. This is a step in the right direction. It is unclear whether the MIL-101 remained porous because of the -NH_2 and -OH functionalization or because the pore sizes in the MIL-101 were larger than those in the PAF-1. This would have been useful to discuss (and might have guided this work a step further toward a different MOF structure for which the overall strategy of lowering the enthalpy of adsorption by metallization might have been accomplished).
- The project goal to achieve physisorption enthalpy in the range of 15–25 kJ/mol appears to be very optimistic. On one hand, the experimental improvements are small (60%) or about 7 kJ/mol, similar to other unmodified porous materials. On the other hand, the computationally predicted Q_{st} values are very high (and unrealistic) for physisorption of molecular hydrogen. There appear to be a significant discrepancy between the theoretical and experimental results.
- Although a substantial amount of work has been reported, the results have been somewhat unfortunate and it does not look like any Program barriers have been overcome. The investigators have addressed some of their own “barriers” by depositing metals inside an MOF. This does not appear to have resulted in a significant increase in hydrogen adsorption, even if a small increase in Q_{st} was observed (from a very low starting value). It would have been good to have seen a better presentation and analysis of some of the data. The data in slide 11 has no legend and so it is unclear whether functionalization has improved hydrogen adsorption. Using values related to the DOE targets (wt H_2/wt material, instead of cm^3/g or mmol/g) would have made the adsorption more readily understandable in relation to the barriers. Also, the adsorption shown on slide 17 is normalized to surface area (although the units are not). Because the surface area of the copper-atomic layer deposition sample was not given, it is not possible to understand the absolute adsorption. The presenter did note this, but it gives the impression that the authors are trying to present the data in the best light rather than show understanding. For these data, perhaps it is possible to compare all of the materials on the basis of moles MOF rather than weight MOF. Maybe both could be given. Because metal:zirconium ratios are known, presumably the surface area, pore size, pore volume, and even adsorption could be compared for the same quantity of zirconium. This would then allow a quick understanding of how the properties have changed as a result of metal addition; for example, how much of the specific surface area change is a result of the increased weight of the MOF. Similarly, it would be good

to know how the increased Q_{st} shown in slide 17 correlates with the amount of copper in the MOF. It is unclear if the inflection or point where the two curves coincide corresponds to the amount of copper.

Question 3: Collaboration and coordination with other institutions

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

- This project features a good range of collaborators from various institutions that are all contributing complementary information.
- The project appears to be well coordinated, and the number of partners and collaborators compares well to the funding for this project.
- This project features good collaboration at the postdoctoral level in the relevant areas of computation and modeling, materials synthesis and modification, and materials characterization, among others. It is likely that the postdoctoral student gained very valuable experience in performing multidisciplinary studies.
- Although many collaborators are listed on slide 18, the contributions of those collaborators are not highlighted well within the technical slides. The technical slides present work primarily accomplished at Northwestern University.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **2.6** for its relevance/potential impact.

- The project is clearly focused on improving the storage capacity of porous frameworks and therefore supports the objectives of the Program.
- The project goal of tailoring the enthalpy of adsorption by metallation with unsaturated metal sites is well within the DOE objectives.
- Improving hydrogen sorption energies beyond what has been shown to be available in conventional sorbents is a goal of the Program's RD&D plan; the potential impact of this project's approach would be very high if a higher heat of sorption could be found at hydrogen loadings of greater than just a few mmole/g material.
- There is significant disagreement between theoretically predicted data and experimentally measured data. It is unclear to which extent the metallation will compromise the storage capacity by increasing the weight of the storage material and decreasing the surface area of the porous structure.
- Although it is evident that more hydrogen can be stored if a Q_{st} of 15–25 kJ/mol is achieved, it is not clear how much hydrogen can then be removed from the system. If a room temperature material can store 7–8 wt.% of hydrogen but only deliver three-quarters or one-half of that amount, it is unclear how these materials are better than cryo-compressed hydrogen. The researchers should see the previous presentations by Dr. Snurr for some data in this regard and present estimates of deliverable hydrogen in the future, directly beside the DOE targets, so that reviewers can quickly gauge the project's progress.

Question 5: Proposed future work

This project was rated **1.8** for its proposed future work.

- The presentation indicates that the metallization leads to decreased surface area. It should be estimated how much the modification of the porous materials compromises the gravimetric and volumetric hydrogen storage densities, both due to the increased mass of the scaffold and the decreased surface area.
- While the project is ending at the conclusion of the postdoctoral student's tenure, the "future work" area was sparse, considering that six months still remain for the project. More details on what the final six months could entail would be useful.
- Even though this project is nearly complete, the "Future Work" section should be treated as what the researchers would do should the project continue, so that future researchers can learn from this work. It is unclear what exactly "iterative materials feedback" entails when the experimental techniques either failed

or resulted in no Q(st) improvement. It is unclear whether the model will suggest new ways to metallate or suggest MOF precursors that will produce larger pore structures that you could not guess on your own.

- Although a clear solution to the problem of MOF metallation has not been achieved (the metallation process still has barriers), the investigators propose to move onward to examining other metals (slide 19 lists more than 60 metals of interest). This does not seem like a logical step forward. The investigators might first try to understand the role (if any) of $-NH_2$ and -OH functionalization in the success of metallation for MIL-101. It is unclear how MOF pore size or surface area affect metallation. These are fundamental questions that should be tackled before moving on to other metals of interest. The study of hydrogen sorption dynamics (in situ) is good future work to pursue.
- The proposed future work was not described especially well and does not appear to be focused on overcoming barriers. It is concerning that insufficient time remains for "Iterative materials feedback" to produce significant results before the project finishes in November 2013. The summary slide indicates that future research will "use computational guidance to further metallate our functional MOF…." It is unclear whether the computation has been shown to make useful predictions in these systems. For example, the start of the presentation shows computed Q_{st} in unnamed MOFs to be -84 kJ/mol for copper; the measured figure was -7 kJ/mol (probably in a different MOF). There are at least three metallated MOFs shown on slide 16. It would seem sensible to compute and measure Q_{st} for all of these to see if the computational method is an accurate predictor before launching into new systems.

Project strengths:

- This project features an exploratory route to open framework materials modifications.
- The project objectives are clearly stated and important to meeting DOE goals for sorbent materials. If successful at developing an approach for adding unsaturated metal sites to MOFs (in order to change the enthalpy of adsorption), this project will have a very large impact on the future of hydrogen sorbent materials. The investigators examine two approaches to metallation. This is very good. The project is challenging because of the loss in surface area on the MOFs after metallation. This barrier was overcome by changing to a different MOF (specifically, a functionalized MOF).
- Some high-storage capacities for materials are under investigation.

Project weaknesses:

- There appear to be a significant discrepancy between the theoretical and experimental results.
- The path forward to developing better materials is not well focused. The project gives the appearance of trying a range of materials to see what works.
- There is poor evidence that theoretical methods will really help MOF development. There was no assumptions slide at the end.
- The investigators should take more steps in the direction of varying MOF type (i.e., pore size) and functional groups.

Recommendations for additions/deletions to project scope:

- The researchers should conduct desorption measurements on metal modified frameworks.