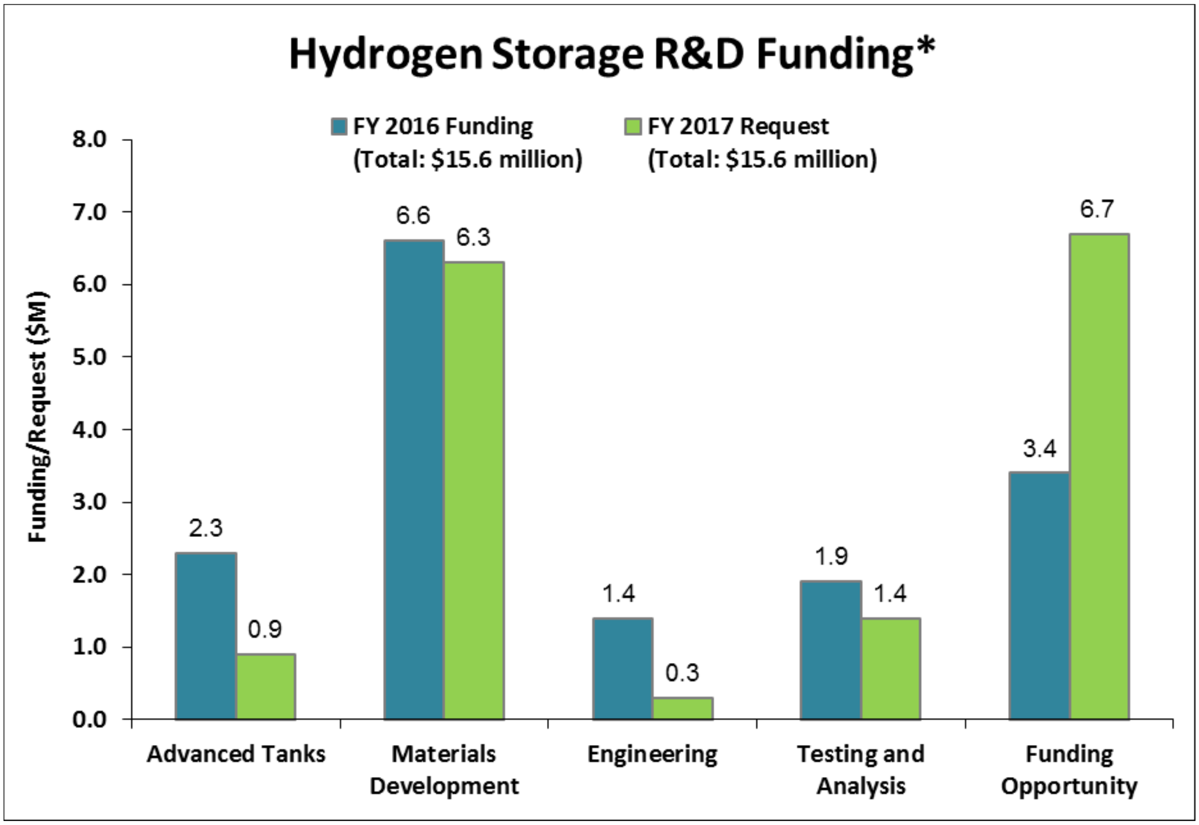
2016 — Hydrogen Storage
Summary of Annual Merit Review of the Hydrogen Storage Program

Summary of Reviewer Comments on the Hydrogen Storage Program:

In fiscal year (FY) 2016, the Hydrogen Storage program portfolio continued to focus on onboard automotive applications through its two-pronged strategy, pursuing strategic near-term and long-term pathways with the potential to meet the cost and performance targets. Reviewers commented that the program is well managed and has been successful in benchmarking progress across its research and development (R&D) portfolio. Reviewers commended the program for ensuring the R&D work remains relevant to the market but also focused on meeting the ultimate targets. The launch of the Hydrogen Materials—Advanced Research Consortium (HyMARC) was cited as one of the program's more notable efforts for the year, and the HyMARC was commended for its emphasis in applying the discoveries from previous materials-based efforts, specifically those from the Hydrogen Storage Engineering Center of Excellence (HSECoE), to address remaining gaps blocking the advancement of materials-based hydrogen storage. With the introduction of HyMARC, reviewers stated the importance of careful coordination across individual projects and related efforts to HyMARC to prevent overlap in activities and maximize results. Reviewers remarked that the program has effectively enabled meaningful collaboration across projects as well as among national laboratories, industry partners, and academia but recommended encouraging partnerships that enable technology commercialization. Overall, the reviewers commented that the program's R&D portfolio is appropriate and comprehensively addresses key technical aspects needed to achieve the ultimate program targets. They noted that greater emphasis should be placed on developing strategies that enable the technology's potential to be commercial in today's market.

Hydrogen Storage Funding:

The chart on the following page illustrates the appropriated funding planned in FY 2016 and the FY 2017 request for each major activity. The program received $15.6 million in funding in FY 2016, and it has a budget request of $15.6 million for FY 2017. In FY 2016, HyMARC, the National Renewable Energy Laboratory-led validation and characterization effort, and various individual projects were launched to advance research on the discovery, development, and validation of novel materials with the potential to store hydrogen and meet the targets. Additional efforts on advanced compressed hydrogen storage systems were initiated in FY 2016.



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

Majority of Reviewer Comments and Recommendations:

The Hydrogen Storage portfolio was represented by 24 oral and 5 poster presentations in FY 2016. A total of 23 projects—via oral presentations—were reviewed. In general, the reviewers' scores for the storage projects were good, with scores of 3.4, 2.0, and 3.0 for the highest, lowest, and average scores, respectively.

Advanced Tanks: Five projects on advanced tanks were reviewed, with a high score of 3.4, a low score of 2.5, and an average score of 2.9. Reviewers considered these projects to be relevant in addressing program needs. For the tank cost reduction projects, reviewers commented favorably on the efforts that employ a good mix of modeling and experiments to validate modeled predictions on cost-reduction pathways through fabrication and testing of real systems, including alternative fiber and resin, low-cost balance-of-plant components, and a novel conformable tank. Reviewers also noted the potential increase in hydrogen capacity offered by cold/cryo-compressed technologies, but they emphasized the need for continued temperature/pressure cycling as well as additional emphasis on the vacuum jacket insulation and related issue of hydrogen dormancy. In general, reviewers recommended more detailed and validated techno-economic assessments. Overall, the reviewers thought the efforts could have a significant impact on the industry.

Materials Development: Fourteen materials-based hydrogen storage projects were reviewed, with a high score of 3.3, a low score of 2.0, and an average score of 3.0. In general, reviewers complimented the unique capabilities developed and technical progress made through the wide range of projects in the program's materials development portfolio. Reviewers commented on the potential of the newly established HyMARC and characterization and validation efforts to address the critical scientific gaps in the field and enable the development of storage materials with a realistic chance to meet U.S. Department of Energy (DOE) onboard storage targets that cannot be theoretically met by high-pressure hydrogen storage tanks. Reviewers agreed that the mix of projects in this area is adequate to address the technical challenges specific to both non-automotive and portable applications.

Reviewers recommended a reduction in work on materials that have already been investigated extensively in previous years and that have not shown any potential to meet the most technical and challenging DOE targets. Material projects will continue in FY 2016, subject to appropriations, and new projects will be initiated. Through close collaboration with the HyMARC and the validation and characterization efforts, new projects will have a stronger link and feedback route between the experimental and theoretical efforts, as well as place more emphasis on meeting projected material-level property requirements to meet the system-level targets.

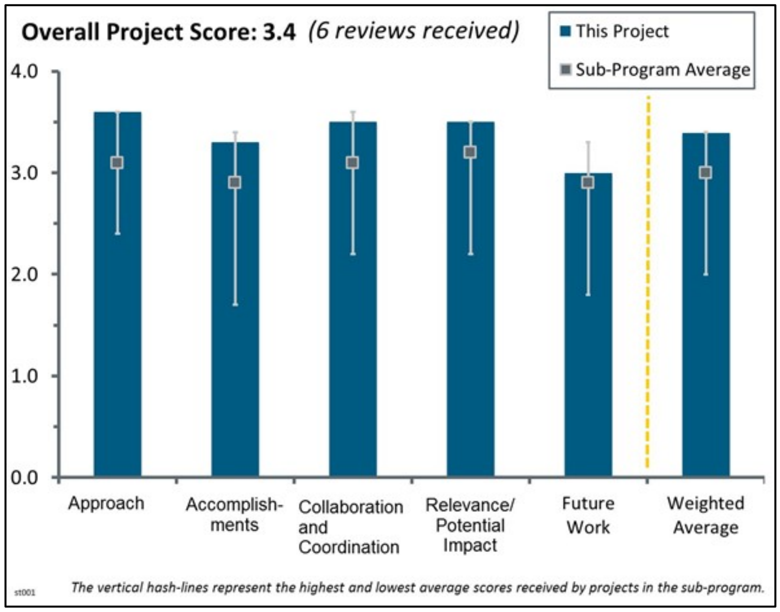
Engineering: Two projects related to hydrogen storage engineering were reviewed, both with a score of 3.3. The reviewers were very satisfied with the approach and accomplishments of the HSECoE and stated that their findings were of utmost relevance to the overall Hydrogen Storage program. They felt that the large group of partners was sufficiently diverse and collaborations were well organized and beneficial for the projects. The reviewers also specified that making the modeling package available to the community was very significant, and that the data obtained on the storage systems will provide a solid foundation for development when a suitable material emerges. The reviewers commended the efforts to enhance the performance and user-interface of the models and stated that it is important to preserve the wealth of information and understanding of engineering concepts and required hydrogen storage material properties developed during the HSECoE.

Testing and Analysis: Two projects related to testing and analysis were reviewed, with a high score of 3.4, a low score of 3.2, and an average score of 3.3. Reviewers stated that these projects are very relevant in assisting DOE's R&D portfolio evaluation. Reviewers commended the performance analysis project for providing unbiased analyses of hydrogen storage options, showing depth in technical evaluation across multiple storage approaches. Reviewers also commended the work on system/material trade-offs, assessing design variations and engineering features for diverse hydrogen storage systems and materials, highlighting areas that either have potential for improvement or are already constrained to current values. However, reviewers cautioned that the assessment of a high-pressure metal hydride storage option needs greater emphasis on overall thermal management issues of the charging performance. For cost analysis, reviewers commended the project's in-depth analysis, including an uncertainty analysis that vets and captures potential cost reduction concepts. Reviewers recommended adding features such as certification costs, tank finishing/rework, and scrap costs to the analyses.

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

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project:



The main objective of this project is to develop and use models to analyze the onboard and off-board performance of physical and materials-based automotive hydrogen storage systems. Specific goals include conducting independent systems analysis for the U.S. Department of Energy (DOE) to gauge the performance of hydrogen storage systems; providing results to materials developers for assessment against system performance targets and goals and for guidance in focusing on areas requiring improvements; providing inputs for independent analysis of onboard system costs; identifying interface issues and opportunities and data needs for technology development; and performing reverse engineering to define material properties needed to meet the system-level targets.

Question 1: Approach to performing the work

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

- This ongoing project continues to provide both DOE and the storage community with valuable systems-level analyses of various aspects of onboard hydrogen storage. This project also serves to validate some crucial areas in which this project and the Engineering Center of Excellence have overlapping tasks. The “reverse engineering” approach has provided valuable input to materials research and development (R&D) efforts; contributed to understanding where costs and mass can be saved in various aspects of physical storage in tanks and in “hybrid” tanks containing metal hydrides, i.e., the Toyota hybrid tank concept; and provides independent validation/review of various aspects of system models developed by other DOE-funded storage programs. It is clear that this effort is enhanced through its other analysis efforts, e.g., the fuel cell analysis program. Having such an excellent background in all of the cross-cutting technologies in the Fuel Cell Technologies Office makes this a particularly valuable team.
- Regarding the approach to performing the work, the principal investigator (PI) provided an overview of two focus areas: analysis of carbon fiber tanks and preliminary analysis of high-pressure hydrides. The high-pressure hydride work is a great example of using reverse engineering to provide some guidance to the materials researchers.
- A logical and innovative approach for development of physical, thermodynamic, and kinetic models has been adopted to understand properties and processes in hydrogen storage systems. The approach also involves the analysis of system/material trade-offs, information that is crucial to developing comprehensive and effective models. The approach is keenly focused on important barriers and obstacles.
- This project serves a very useful role by independently assessing design variations and engineering features for diverse hydrogen storage systems and materials. While this information does not explicitly contribute to possible improvements in hydrogen storage systems, it does highlight areas that either have potential for improvement or are already constrained to current values. Most major factors have been considered and also reevaluated during the nearly eight years the project has been ongoing. Hence, even though the approach remains sound, it is not clear whether significant novel options can result.

- Use of the Abaqus modeling tool has provided helpful guidance for estimating key hydrogen storage system performance metrics.
- The project provides valuable, unbiased analysis of various hydrogen storage options under consideration by DOE.

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.

- During the past year, the Argonne National Laboratory (ANL) team continued assessing alternative configurations for Type IV 700 bar tanks, where most variations were found to have relatively minimal impact on increasing performance levels against the DOE targets. It was most interesting to see ANL's evaluation of the Toyota Mirai storage vessel when compared to U.S. domestic designs. While Dr. Ahluwalia stated during the question-and-answer portion that the 40% mass reduction claimed by Toyota was for a non-optimized baseline tank, the ANL results indicated a much smaller improvement to current (quasi-optimized) vessels being used in other vehicles. The new task for evaluating high-pressure metal hydride vessels with a 350 bar operating pressure was very comprehensive, but it was difficult to extract the key results with regard to requirements being necessary to match performance of a 700 bar compressed gas tank. Although a number of properties were rapidly covered via multiple figures, summarization of metal hydride was rather sketchy and should be clarified.
- Solid progress has been made in all project areas: physical systems, high-pressure metal hydrides, sorbents, and chemical hydrogen systems. Especially noteworthy results include (1) establishment of new performance metrics for 700 bar hydrogen tanks, (2) development and validation of improved tank design concepts, (3) identification of potential ways to reduce the quantity of carbon fiber and resin in compressed gas tanks, and (4) analysis of thermodynamic requirements for high-pressure, low-enthalpy metal hydrides capable of enhancing the performance of compressed hydrogen tanks. These are all important results that have an impact on DOE decisions about hydrogen storage system development.
- This project continuously provides valuable feedback, validation, and review of a wide-ranging array of technologies surrounding the multiplicity of approaches to onboard hydrogen storage. This requires chemical engineering, mechanical engineering, and cost analysis techniques, among others, and this team carries out the application of these various analyses very well.
- Very good progress has been made related to the hybrid high-pressure tank and 700 MPa Mirai system.
- The project showed depth in technical evaluation across multiple storage approaches.

Question 3: Collaboration and coordination with other institutions

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

- Extensive collaborations with national laboratories and several private companies and original equipment manufacturers are enhancing the impact and progress in this project. This project has been carried out successfully over the last several years, and it is apparent that the close collaborations between the PI and cooperating partners have augmented the total effort.
- This ANL team does interact well with the other organizations via both effective interchanges of technical inputs and communicating the team's outputs.
- Without superior collaboration, this project would not succeed. Because it does succeed exceedingly well, it follows that the collaboration among the various projects within the Hydrogen Storage program and the ANL analysis effort must be outstanding.
- The project contains a comprehensive list of partners and is well positioned to meet the scope of the program goals.
- Current activities did not have external collaborators looking at materials. The project was more focused on directions from DOE on analysis of Type IV tanks and new concepts in high-pressure materials to learn whether there are new opportunities to explore.
- There is visible collaboration with other institutes.

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

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

- This project is unique in the DOE portfolio; i.e., as stated in the presentation, “project continuation and direction is determined annually by DOE.” Based upon the project’s long-standing success and continuing DOE support, it is readily apparent that the project is critical to the Hydrogen and Fuel Cells Program (the Program), and it is clearly advancing progress toward achieving DOE goals and objectives.
- The project is very useful in obtaining hydrogen storage performance metrics that help evaluate existing storage methods and possible improvements that could be implemented.
- The technical and cost review and analysis offered by this project serve as valuable tools for vetting various hydrogen storage approaches so that investments can be placed where payoff is highest.
- Without the feedback from these analyses and reverse engineering efforts, the materials and physical-based storage projects could not be as effective.
- The potential of this effort for generating novel improvements is likely limited because most variations for hydrogen storage systems have been considered. From current and past analyses by the ANL project and others, there are virtually no known solid storage media candidates that can simultaneously satisfy the 2020 DOE targets, let alone the ultimate values. ANL and others have found over the past decade that the variety of design features is always a compromise of contradictory requirements and behavior for either physical or chemical storage systems. Perspectives for finding a breakthrough system simultaneously meeting all 2020 vehicle targets have low probability.

Question 5: Proposed future work

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

- The proposed future work on physical and materials-based storage follows logically from the current effort. The project team clearly recognizes the importance of terminating activities as needed and documenting/publishing relevant R&D results. The continuing focus on physical storage is appropriate. New results and understanding of emerging material systems will be derived from the consortium projects led by the Hydrogen Materials—Advanced Research Consortium (HyMARC) and the National Renewable Energy Laboratory, and it is anticipated that as these results become available, they will be used to guide future work in this effort.
- The project is doing excellent work to help others better understand materials needs from reverse engineering of systems. The team should keep up efforts to publish results in a timely fashion.
- The future plan is very good.
- In many ways, the analysis efforts are tied to the Hydrogen Storage program needs, so it is understandable that sometimes this project has future plans that are “to be decided.” What is presented as future plans is logical. There may be some need to re-examine whether the future effort in high-pressure metal hydrides is the best use of ANL resources, as the initial analyses appears to indicate that there are no known materials that have the desired properties.
- Future work should include not only technical review but also market opportunity and guidance for potential future supply chain investments. The Institute for Advanced Composites Manufacturing Innovation’s commercialization efforts require a techno-economic model to drive industry investments.
- There should be less emphasis on continuing the analyses of Type IV 700 bar storage vessels and more attention paid to an enhanced scope of treatment on solid storage materials.

Project strengths:

- This ongoing project has been making valuable contributions to the Hydrogen Storage program for several years. The PI and his team provide DOE with expert and timely systems analysis of problems directly relevant to both the short- and long-term needs of the program. Independent analysis of this kind is a valuable component of the overall Program.

- This is an excellent team with a long history of contributions and of doing important work for the Program. The team is highly skillful at addressing a variety of types of engineering analyses. At times, the “reverse engineering” approach may appear to be too general, but the project continues to provide valuable insight to those who need it most: the researchers.
- The ANL team has developed and implemented a variety of models for assessing and predicting the attributes and limitations of nearly all types of hydrogen storage systems. The team provides valuable constraints required from various storage media.
- This is an experienced team that works hard to provide insight into many if not all of DOE’s projects.
- The approach and concepts are useful and have been validated on some occasions.
- The project was comprehensive in review of ongoing technical work.

Project weaknesses:

- Given the current status of metal hydride and chemical hydrogen storage materials, continued work on systems that employ those materials is probably not appropriate, and it is diluting the overall impact of the project. The project should be sufficiently “nimble” to straightforwardly accommodate analysis of those systems as improved materials emerge in the future. (Note: this is not really a “weakness”—the project team should consider it as an observation/recommendation.)
- Because the ANL team does not have resources for direct experimental characterizations and verification of hydrogen storage candidates, the team must rely upon literature and other outside sources for input parameters during the system analyses. Often critical property values are either not available or are unreliable, which can have an impact on the predicted results. It should be noted that only a couple of candidate metal hydrides occupy the desired enthalpy–entropy region in the figure on slide 14. The team should actively seek out experienced researchers both to provide sources of other data and to participate in periodic detailed technical discussions and review to critically adjudicate the project’s predictions.
- The project does not make suggestions for further technical work that would help establish business opportunities for further investment.
- The project is modeling-based and uses several assumptions.

Recommendations for additions/deletions to project scope:

- One of the general outcomes of the Engineering Center of Excellence was a recommendation of materials that had a targeted enthalpy in the range of 20–27 kJ/mol H_2. It would be interesting to see a similar analysis of the entropy range that would be necessary to meet DOE targets based on equilibrium pressure needs and kinetics—similar to what was performed for the high-pressure hydrides presented at the Program’s Annual Merit Review. It is understood that the Program needs to find storage solutions across all vehicle platforms. It would be optimal to have a “single” solution; however, perhaps a reverse engineering approach could provide some guidance about differences between an optimized system for small/subcompact vehicles on the one hand and large sport utility vehicles on the other hand. The high-pressure hydrides might work for certain vehicle classes better than others. Chemical hydrogen storage (CHS) provides an approach to some of the highest gravimetric and volumetric density of hydrogen, yet CHS faces significant challenges for onboard storage from an engineering need. Given the high volumetric and gravimetric density, perhaps there are some findings of the reverse engineering performed on CHS for onboard storage that could be transferred—or considered—as an approach for hydrogen delivery.
- In light of the minimal improvements found during the past few years for the nominal 700 bar compressed hydrogen vessels, further systematic analyses are not recommended because little payback can be expected. On the other hand, the suggested evaluations (presumably comprehensive of onboard and off-board behavior) of cryo-compressed vessels for fleet vehicles should be worthwhile. The assessment of the high-pressure metal hydride storage option needs to be completed with greater emphasis on overall thermal management issues for the charging performance and requirements on the manufacturability and hydrogen-charging infrastructure. A more in-depth comparison of optimized Type III versus Type IV vessels for hydride-base tanks should be made to see which has the better adaptability and lowest cost. The team should make clear the benefits, limitations, and trade-offs necessary to achieve optimal efficiency and economic value. As an example, if the cost of producing and processing the metal hydride alloy is greater than the cost benefits from reducing 45+ kg of high-strength carbon fiber for the vessel containment, there

appears to be little incentive to consider hydride tanks over 700 bar compressed gas vessels other than niche applications.

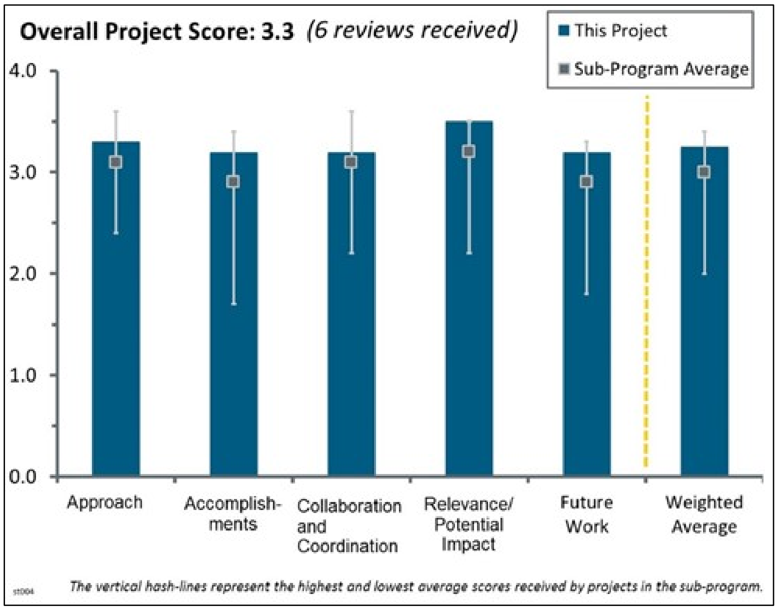
- Having another look at the hybrid tank issue is interesting, and perhaps this comes from the Program management, but it is not clear that there is hope for this approach—or perhaps it was not clear from the presentation what the justification is for this aspect of the future project.
- The project should de-scope work on metal hydrides and chemical hydrogen systems until reversible material candidates that at least approach the DOE storage performance targets emerge.
- The project can make suggestions for further technical work and help establish business opportunities for further investment.
- Including some sensitivity analyses of key parameters is recommended.

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

Don Anton; Savannah River National Laboratory

Brief Summary of Project:

Using systems engineering concepts, this project's goal is to design innovative materials-based hydrogen storage system architectures with the potential to meet U.S. Department of Energy (DOE) performance and cost targets. Savannah River National Laboratory (SRNL) will develop and validate system, engineering, and design models that lend insight into overall fuel cycle efficiency. All relevant materials data for candidate storage media will be compiled and required materials properties defined to meet the technical targets. SRNL will also design, build, and evaluate subscale prototype systems to assess the innovative storage devices and subsystem design concepts, validate models, and improve component design and predictive capability.



Question 1: Approach to performing the work

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

- The participants of the Hydrogen Storage Engineering Center of Excellence (HSECoE) demonstrated that the HSECoE approach is a very valuable construct to move very difficult, complex problems forward. The materials-based hydrogen storage area is one of those very difficult problems that have benefited tremendously from the HSECoE approach that brings the best expertise to bear on a set of problems. The presentation outlined one such example: comparing and contrasting the engineering issues and systems issues surrounding the potential utility of adsorbent materials operating at sub-ambient temperatures. The HSECoE provided a very systematic look at two different adsorbent system configurations, which yielded interesting details of the pros and cons of each approach and the impacts on system design and their relative abilities to meet the DOE targets. The failure mode and effects analysis (FMEA) approach the HSECoE adopted from original equipment manufacturers (OEMs) also provided an engineering culture method to demonstrate how project prioritization was helping to more effectively achieve project goals. In the end, the engineering assessments and modeling approach provides critical input to the "next generation" of materials-based storage projects, e.g., the Hydrogen Materials—Advanced Research Consortium (HyMARC).
- The approach, which builds on years of prior work in the HSECoE, combines experimental testing of two heat exchanger systems with detailed heat transfer modeling of these. The integration of these is very good, allowing models to be validated.
- This is a long-term project conducted in a very systematic and professional manner. The project significantly contributed to identifying and helping to solve critical barriers.
- The approach describes aspects of the work that were covered in 2015, but given the nature of the no-cost extension and the fact that this project was initially designed to end last calendar year, this is not surprising. Somewhat more data on the modular adsorbent tank insert (MATI) system was presented that described cycling characteristics, noting that no degradation of capacity was seen.
- This project is concluding in 2016. The approach during this reporting period focused on addressing remaining adsorbent engineering issues—mainly completion of the MATI and Hexcell heat exchanger work. This is important because it provides the basis for down-selecting an optimum heat exchanger for

adsorbent systems for the final prototype storage system. The approach is straightforward and is keenly focused on characterizing and evaluating the two heat exchangers for practical system applications.

- The HSECoE was initially tasked with developing onboard reversible hydrogen storage systems. Although the initial goal was to engineer prototype tanks for all three main classes of hydrogen storage systems, the majority of the research efforts were focused on designing and engineering cryogenic Hexcell and MATI sorbent tanks. The future plans include tests under more realistic conditions of temperature for a practical sorbent system (160 K and above), yet the tests on prototype systems were performed exclusively at temperatures between 80 K and 90 K.

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.

- As this Center of Excellence wraps up, the work presented demonstrated good to excellent progress toward its final goals, particularly in the sorbent system work, and in ensuring that the enduring online access to the models is maintained and that the models are now more "user-friendly." Without providing for an enduring "online presence," the HSECoE would not have the desired impact. Therefore, the progress is good to excellent.
- Solid progress was achieved on evaluating the MATI and Hexcell heat exchanger options or adsorbent materials. An especially noteworthy result is that a system employing MOF-5 adsorbent pucks compacted within a MATI heat exchanger in a Type I tank exceeds the volumetric and gravimetric capacity obtained from compressed hydrogen at 700 bar in a Type IV tank. However, a higher-temperature metal–organic framework (MOF) is needed, and the small performance advantage obtained with the current MOF-5/MATI system is likely outweighed by the complexity of that approach compared to the compressed gas option. The FMEA for an engineering system comprising MOF-5 adsorbent in MATI and Hexcell heat exchangers provides useful information concerning limitations of the two options in a practical, real-world storage system. Likewise, the clear articulation of remaining sorbent engineering issues and obstacles provides a focus for future work. Overall, even though an optimum material system meeting all DOE targets was not available, the HSECoE team has done a first-rate job of developing and evaluating engineering subsystem options that incorporate the principal classes of emerging materials systems.
- Of most value was the assessment that, while short of DOE requirements, the material class of promise was adsorbents. While the development of new materials or materials systems cannot be anticipated, lack of information on costs associated with forecourt delivery requirements at low temperatures is lacking (and outside of the scope of the HSECoE). Some guidance from DOE on the practicality of low temperature from a cost standpoint may be required in order to fully gauge the practicality of such systems. Given the present limitations of other materials, especially complex hydrides, in requiring high temperatures for significant hydrogen release, adsorbents may be the only game in town. The work describes some of the difficulties encountered with the substitute MATI system that suffered from brazing issues and so did not fully reflect engineering data of an optimized heat transfer design. The personnel changes at Oregon State University that were mentioned are unfortunate. Whether this was a student who graduated or technical help that moved on, some contingency would have been of value.
- The project accomplished much-needed analysis and experimental objectives over its seven-year lifetime. However, after considerable monetary expenditure, the MATI and Hexcell systems were shown to (potentially) perform only slightly better than compressed gas. The project was able to demonstrate this potential and thus was a success. However, in the end, a new form of hydrogen storage with significantly improved performance was not identified.
- The main accomplishments seem to be in the area of modeling the physical hydrogen storage behavior in materials. The predictive models of evaluating the impact of various parameters and physical properties of materials on the technical targets are certainly valuable. Unfortunately, most of the models were not validated experimentally. For the prototype systems built based on MOFs, the main efforts were focused on probing the behavior at cryogenic temperatures, which scientifically is of interest, but unfortunately, it is far from the technical targets of a practical storage system. It is regrettable that no tests were performed under more realistic temperatures.

- Milestones were mostly met for the Hexcell system but not for the MATI system (modeling is incomplete at this stage). This is understandable, however, in light of the problem with the brazing on the initially delivered MATI unit. A manufacturing defect was discovered (brazing had wicked into passages in the MATI and blocked nitrogen flow). Off-line non-destructive evaluation (NDE) analysis revealed this problem. Although unanticipated, identification of this problem provides a useful heads up for future manufacturing involving this design. A large array of tests was done for both subscale systems and the full 2 L adsorption unit, providing a substantial body of data for model validation. Cycling tests also help to understand system performance under realistic conditions as well as repeatability and durability. Remarkably good agreement of experimental data with models is found. For Hexcell discharging, the team had to periodically shut off hydrogen flow because the system was heating too much. It is not clear whether this is a design flaw that needs to be fixed. The full-scale Hexcell system would produce 3.2 wt.%, and the MATI system would give 3.1 wt.% (surpasses 700 bar tank). The team completed the FMEA and developed the full-scale Hexcell system design concept, and the model is complete. All reviewer comments from the previous DOE Hydrogen and Fuel Cells Program (the Program) Annual Merit Review appear to have been adequately addressed.

Question 3: Collaboration and coordination with other institutions

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

- Without great collaboration among participants and with project management, the HSECoE would not have succeeded. As the HSECoE did succeed, the collaboration must have been excellent.
- The team tied together numerous institutions in a productive manner. The team was sufficiently diverse to provide adequate representation of skills and points of view.
- Although collaborations were not summarized in this final presentation, extensive and highly beneficial collaborations and cooperation both within and outside the HSECoE have enhanced the progress throughout the duration of this project.
- This is a large team (13 organizations). From the presentation, it was not clear what the role of each partner is, although logos on various slides indicate contributions from organizations outside SRNL. It does not appear that all of the partners are still contributing, but considering that this year was an extension of the project, this is understandable.
- There seems to be good collaboration and coordination within the HSECoE, but not much communication and collaboration with outside institutions and principal investigators.
- This effort was originally set up with a number of collaborations in place. There appears to have been some difficulty with the speed with which implementation and feedback among various institutions could take place. For projects of this type, design and construction of various components may have been better off had they been outsourced.

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

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

- The relevance of an engineering center of excellence to DOE goals could not be greater. There is no higher calling within the Program than to provide systems-level analyses and feedback to current and future materials-based efforts. As the HSECoE succeeded in providing such feedback through analyses and through various system-level models that have been or are nearly complete, it has provided an outstanding degree of technical impact.
- The information that was gleaned from the HSECoE activity offered valuable data on systems and designs of potential interest and was especially valuable in highlighting materials requirements needed to achieve the range of metrics as demanded by fuel cells.
- This project was a logical follow-on to the various materials centers of excellence and has generated a great deal of useful practical information. In addition, modeling tools and data are being made available for others to use through the HSECoE website, enabling the impact to extend beyond the HSECoE partners.

Engineering challenges remain, but it is likely that further significant progress will depend on the identification of a material that can meet the DOE targets.
- This is clearly an important project for the Hydrogen Storage program. It provides a solid foundation for development of engineering prototypes and storage systems in the future.
- This HSECoE effort is relevant to achieving the DOE technical targets as it provided important guidance for the materials discovery efforts. The potential impact could have been even higher if the prototype systems were tested under more realistic conditions of temperature and hydrogen pressure for practical sorbent systems.

Question 5: Proposed future work

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

- The work that remains is to complete the modeling work in a way that makes the package generally available to the community, and the plan for completing this is hopefully on track.
- As this is the closeout, this category is not terribly applicable, but to the extent that the HSECoE has provided for enduring access to its online information and models, its contribution is excellent.
- The remaining engineering issues were clearly summarized. Some materials-related issues also exist (e.g., compaction of MOFs), but identifying a specific material to focus on should come before investing a great deal of effort into these.
- There is some value in finishing up the proposed modeling work. However, it is suspected that the models will only be useful to the team if research activities related to MATI/Hexcell continue. If they do not, the models will likely be a waste of time.
- The future proposed efforts seem to be exclusively focused on sorbents. It would be desirable to include modeling of other classes of hydrogen storage materials, such as chemical hydrides and reversible metal hydrides.
- The reviewer did not score this area—the project is concluding in 2016 (except for ST-008 on documentation, testing, and enhancement of storage system models). Consequently, a review of future work is not really relevant. However, the HSECoE team has provided an excellent summary of remaining issues and obstacles that affect successful development of an engineering prototype. These can be viewed, at least in part, as a good basis for a possible follow-on effort in the future.

Project strengths:

- Project strengths include the well-organized, multidisciplinary team involving laboratories, industry, and OEMs. The project has a good combination of experiments and modeling. There is a concerted effort to make results widely available.
- The HSECoE is, overall, well organized. The research efforts have been focused on addressing the most significant engineering challenges associated with developing materials-based hydrogen storage systems for hydrogen vehicles. The main strength of the project is that it accomplished one of the original objectives in designing and evaluating prototype solid-state hydrogen storage systems; the data obtained for sorbent systems seem to be the most useful for future research and engineering efforts.
- The project combines both theory/modeling and experimental/engineering components in a synergistic way. The project team is well qualified to conduct the engineering and development work on this project. The project is well managed, and extensive collaborations and cooperation are evident.
- This is a professionally executed and complex project.
- Project strengths include the collaboration, great team, systematic approach, detailed analyses, and accepted feedback from multiple stakeholders. It took a while, but this Center of Excellence turned out okay.

Project weaknesses:

- In the end, there were none.
- No significant ones are identified.

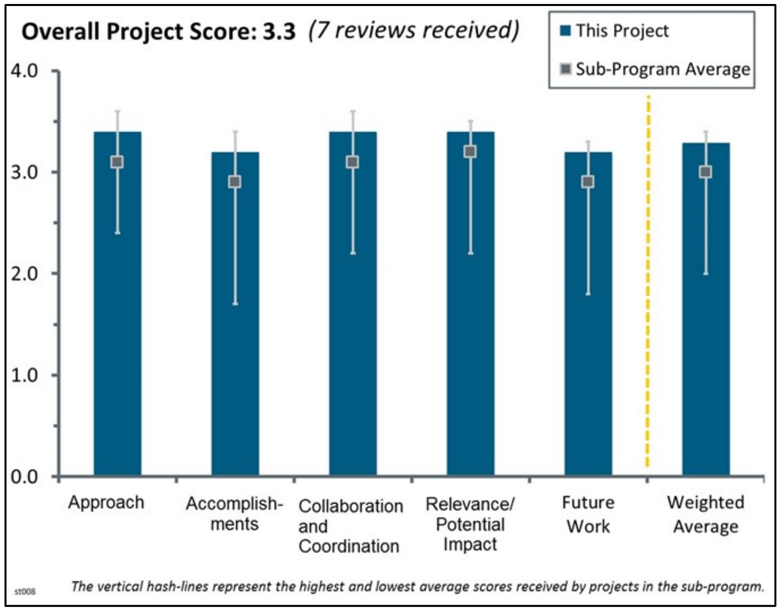
- As noted both by reviewers and by the HSECoE project team members, the overarching weakness was the lack of a storage material capable of meeting DOE targets. Despite that, the HSECoE team did an excellent job of evaluating existing materials and developing engineering subsystems that employ the best candidate materials that are currently available. That work provides a solid foundation for development of an optimized engineering system if/when a suitable material emerges.
- The HSECoE seemed to lack a comprehensive and well-defined research plan. Certain areas of research, such as thermal energy management, seem to be studied rather extensively; but some other areas, such as materials compatibility, potential reactivity (especially for metal and chemical hydrides), and hydrogen purity, remain poorly understood and require more investments. It is quite difficult to sort-out why certain particular compounds (instead of others) were selected for study. The approach seems semi-random; no justification was given for why certain research activities were prioritized versus others.

Recommendations for additions/deletions to project scope:

- The sorbent hydrogen isotherm data fitting effort is valuable and should be continued. It would be desirable to expand the models to other classes of hydrogen storage materials, such as reversible metal hydrides.
- The project should consider whether completion of the modeling efforts is needed. Performance data for 100 L/minute and 500 L/minute are reported for the Hexcell system. However, the station impact of these two flow rates should be assessed.
- The project is ending in 2016. Consequently, there are no recommendations for revision of project scope.

Project #ST-008: Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements

David Tamburello; Savannah River National Laboratory



Brief Summary of Project:

The ultimate goal of this project is to provide and enhance publically available material-based hydrogen storage system models that will accept direct material property inputs from material developers to accurately predict material-based hydrogen storage system performance. In support of that goal, this project maintains, enhances, and updates the Hydrogen Storage Engineering Center of Excellence (HSECoE) hydrogen storage system modeling framework and model dissemination web page.

Question 1: Approach to performing the work

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

- Managing and documenting the models developed in the HSECoE project is critical to ensure that the project continues to have an ongoing presence and impact in future years. The approach adopted in this project provides an effective means for external investigators to access and employ HSECoE models in a straightforward way. Several useful models and simulation modules and frameworks have been developed. The approach successfully addresses the multiple challenges underlying successful development and deployment of those models. The project will provide investigators with the opportunity to input new materials properties and to assess the associated system characteristics. This will be an important legacy of the HSECoE effort.
- The approach sounds practical and user-friendly. It is good to see there is a focused effort to distribute results of the HSECoE and maintain their availability, which is always a challenge after a project ends. The ultimate goal of allowing users to input their own material property data is excellent.
- This project is an extension of a portion of the HSECoE consortium effort that is continuing and updating the predictive modeling techniques for alternative hydrogen storage media (e.g., metal hydrides, chemical hydrogen, and adsorbents) with some complementary baseline models for compressed gas storage. This task is currently focused on performance enhancements of example media by allowing impact of varying relevant materials properties within specific storage vessels evaluated during the HSECoE project. In essence, these online models should allow outside users in the international hydrogen research and development community, who possess the appropriate software, to make comparisons over a range of parameters and operating scenarios against reference materials. The objective is to assist these researchers to identify viable candidates with the potential to meet the U.S. Department of Energy (DOE) vehicle performance targets. The project will continue provide a level of technical support to the model website to assist outside users.
- Ongoing efforts are focused on making “models” for sorbents and chemical hydrogen storage materials available to the research community to provide a rational approach to compare different materials and better understand how different materials properties will affect vehicle performance.
- The approach helps scientists and engineers to identify opportunities and challenges with materials from tank and system points of view.
- This presentation represents the completion or near-completion of vehicle modeling for various materials categories, accomplished with a somewhat limited data set based on available materials.

- The relatively easy-to-use modeling programs are the best possible means by which to make the conclusions of the HSECoE available to the materials hydrogen storage community. The project lacks an effort to obtain feedback from users and then to make appropriate adjustments to better facilitate use.

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.

- Overall accomplishments are substantial and address the needs of potential users. Good progress is being made on all models, and website support, access to document models, and data are provided, including user manuals. Available codes include a metal hydride acceptability envelope. The project is also providing a framework model with physisorption and metal hydride storage, etc.; a chemical hydride storage model and tank volume/cost model (raw materials only); sorbent models that will be made flexible to consider materials other than metal–organic framework (MOF)-5 (the same for the chemical hydrogen storage model); and a model that allows one to assess the quality of isotherm data and show where additional data are needed. This progress is remarkable considering the relatively small amount of funding for the project.
- Good progress toward all project and DOE goals was made in this reporting period. A large number of varied and useful storage system models either have been posted or are projected for release in the near future. The models are being updated and validated as needed. Good progress has also been achieved on developing and testing a comprehensive hydrogen vehicle simulation framework. The project team is working to make the user interface as “friendly” as possible, ensuring that the models will find wide acceptance in the hydrogen storage and fuel cell electric vehicle communities.
- This project started officially at the beginning of fiscal year 2016 and is making steady progress in updating, refining, and maintaining the HSECoE model dissemination website. Steady international interest and activity with the website was indicated from the tracking statistics given during the DOE Hydrogen and Fuel Cells Program Annual Merit Review presentation. Plausible comparisons between the adsorption system models and the laboratory tests on the two configurations for the storage beds were shown, along with scale-up for modeling full-size beds (i.e., circa 5.6 kg of hydrogen capacity). Nevertheless, both the HexCell powder and Modular Adsorption Tank Insert pellet systems fail to meet the desired 2020 targets. Simulations are helpful tools in understanding behavior but may not hasten discovery or development of the specified targets.
- The software capabilities developed at this stage allow for exploring different materials, apart from adsorbents.
- Excellent progress has been made. The development of the modeling programs appears to be on track.
- There is strong collaboration between laboratories to make models “user-friendly” for researchers developing new materials for onboard storage.
- At present, the model relies heavily on MATLAB. One hopes that enough documentation will eventually be provided to better judge the transparency of the code. As it stands, the data that were presented appear adequate in projecting the performance of the two adsorbent designs that were ultimately built.

Question 3: Collaboration and coordination with other institutions

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

- Team members from different nations, as well as outside members, had very close interaction with a number technical interchanges throughout this project. The modeling programs and operating software are the results of dedicated team effort between the laboratories, reflecting excellent collaboration.
- The three laboratories appear to be collaborating well. It is difficult to gauge the actual extent of the interactions, but judging from the extensive results presented, these interactions are occurring and are effective.
- This project on modeling is one of the best examples of how collaboration can lead to accelerated progress on a complex, challenging problem.
- Close collaborations among several partners in the HSECoE are evident. The project is managed and coordinated well. The collaborations are clearly augmenting the overall progress.

- There is visible collaboration among other stakeholders at the HSECoE.
- There is a strong collaboration among team members. Effort should include “outside” users that are not former HSECoE members.
- This effort relied on input from University of Quebec at Trois-Rivieres and Oregon State University in order to validate the models used. Otherwise, the effort was conducted for the most part within Savannah River National Laboratory with some outside testing by project consultants.

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

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

- The website is attracting good attention—it looks like there are ~200+ regular users. Codes are being downloaded, although it is not clear how (or whether) they are being used. Nevertheless, the access numbers indicate that there is serious interest in the information and tools that are available here. Kudos to the team for enabling this user-friendly access. This high level of interest is also testament to the significance of the results achieved by the HSECoE.
- This project is an important adjunct to the overall technical effort in the HSECoE. Proper documentation and distribution of user-friendly models developed in the HSECoE project are essential to ensure that the project has an impact on future development and testing of engineering systems. As such, the project strongly supports the goals and objectives of the DOE Hydrogen and Fuel Cells Program.
- Ultimately, the HSECoE’s relevance will be determined by the extent to which results from the center are utilized by future investigators working on the development of hydrogen storage materials and materials-based hydrogen storage tanks. Thus this project is key to the success of the HSECoE.
- Overall, this work will be useful in making available the HSECoE models and results to the general hydrogen storage community, and one hopes the work will provide a legacy by enabling transfer of engineering concepts and materials properties during the development of improved materials-based hydrogen storage systems.
- Identifying materials limitations from system point of view would aid the community in proposing new concepts and solutions to overcome existing challenges up front.
- While there appear to be a number of visitors to the site, the overall impact is difficult to discern, as the original equipment manufacturers presumably have in-house means of assessing the performance that they require.

Question 5: Proposed future work

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

- Continuation of this effort beyond the conclusion of the core HSECoE activity will involve maintaining and enhancing framework models and beta testing and posting of selected models. The plans and milestones are straightforward, and they follow logically from the solid work conducted thus far on the project. An important aspect will be the publication of the work (especially underlying assumptions) in widely read journals (i.e., in addition to project descriptions provided in the final report).
- On slide 24, the team succinctly outlined the planned future activities and objectives. These are all worthwhile and reasonable within the funding allocated to this effort. The reviewer concurs with the sequence of effort and intent of the specific tasks. An important aspect of this task is to document fully the support manuals for these documents along with providing detailed example test cases for the outside user to establish correct procedures during analyses.
- The plan is for this effort to provide an executable from the original MATLAB code and to make this available with an Excel interface for user-provided inputs. This seems to be the best approach for completing this effort.
- Future work will include stand-alone fitting routines, adsorbent model updates, and versions of codes that do not require users to have MATLAB. A remaining challenge that was not addressed in the presentation is

what happens after funding for this project ends and who will maintain the website. Changes to servers and associated software can lead to links breaking and codes not functioning properly.

- The planned future work, which includes maintaining the webpage and supporting the users, is good.
- Future plans are on target, except that there are no plans to obtain input from “outside” users and no plans to make adjustments to make utilization of the modeling programs easier for “outside” users.

Project strengths:

- A highly capable team has been assembled to conduct the technical effort on this project. The team understands the need to develop models that are effective and powerful but are also are user-friendly (beyond MATLAB). It is apparent that careful thought has been devoted to proper documentation of the models and consideration of how the models might be enhanced and adapted for use with emerging new materials.
- A great strength of this project is that the core team members have extensive knowledge and expertise of all of the hydrogen storage media as well as the appropriate software and analytical packages to develop and execute the modeling codes for the website. This is an ideal collection of experienced individuals to continue and extend the HSECoE objectives. The remaining challenges and barriers as summarized on slide 26 demonstrate that the team recognizes several key areas that need to be addressed to produce better materials-based hydrogen storage systems.
- The project is developing very useful tools based on the results of the HSECoE for the materials-based hydrogen storage community within the allotted time frame.
- The project allows the public to make use of the vast amount of knowledge generated through the HSECoE.
- This is a strong, effectively collaborating team with a clear vision and understanding of its mission.

Project weaknesses:

- Probably the most significant limitation is that the current detailed models are written in MATLAB/Simulink or Comsol computer codes that are not universally available for many materials researchers. Hence, these models being developed and made available on the website may not be sufficiently utilized to evaluate new candidate materials or storage systems.
- Outside materials developers would find it useful to have access to the source codes so that they could be modified if needed. This access is currently not available.
- Model validation is always a concern. It is unclear how the core models and model enhancements will be validated in the absence of an ongoing HSECoE engineering activity.
- It is unclear how online information and the website will be maintained in the future.
- No “outside” user feedback is being obtained.

Recommendations for additions/deletions to project scope:

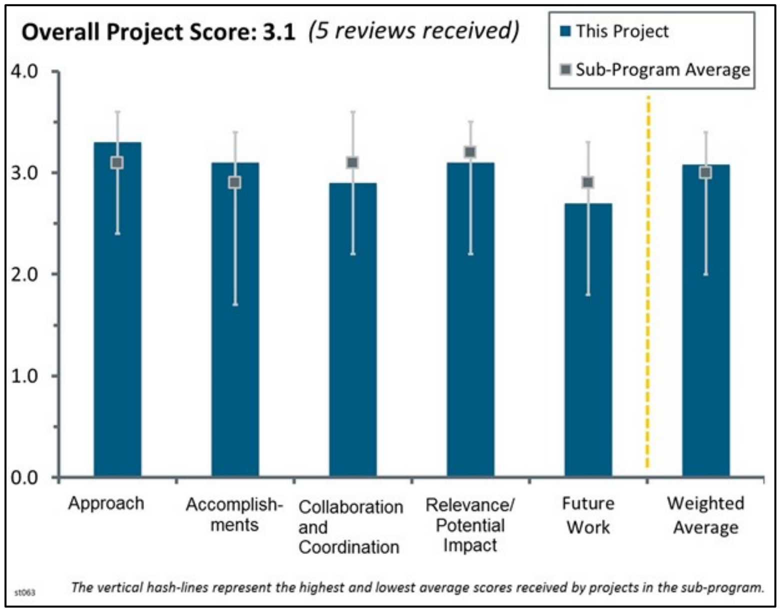
- It is not clear whether the current model for the sorbents works well for materials being designed to operate near ambient temperatures. The model may need to be modified to allow researchers to look at sorbent materials that have sufficient binding energies that they do not require liquid nitrogen. It could be valuable to host a workshop once or twice per year demonstrating how to use the model with input from a couple “outside” users. For example, someone could demonstrate how the model is supposed to work using a material that has been investigated in the recent past, showing how to input the critical material property parameters and what the output looks like for a given material—and maybe even include a sensitivity analysis that would show which parameters are more sensitive to minor modifications.
- It will be important to publish the results of this work in relevant and widely read journals. An essential element of the publication(s) must be a discussion of critical assumptions that have been made in development and implementation of the models. References to the publications should be included in the website.
- The issue of website and data availability beyond 2018 (project end) should be addressed. The project should consider making the codes and manuals available independently from the Internet, such as on a compact disc (CD) or memory stick.

- In general, the outlined scope for this project is appropriate and should be feasible to accomplish. Thorough documentation of the instructions for the downloadable computer models should be provided, and including specific software requirements and limitations is very desirable.
- The project should obtain feedback from “outside” users that are not former HSECoE members and then make adjustments based on their input.

Project #ST-063: Reversible Formation of Alane

Ragaiy Zidan; Savannah River National Laboratory

Brief Summary of Project:



The overall goal of this project is to develop a low-cost rechargeable hydrogen storage material with cyclic stability, favorable thermodynamics and kinetics, and high volumetric and gravimetric hydrogen density. Specific objectives include (1) development of cheaper techniques to synthesize alane, which avoids the chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl or NaCl; (2) utilization of efficient electrolytic methods to form AlH_3; and (3) development of crystallization methods to produce alane of the appropriate phase, crystal size, and stability.

Question 1: Approach to performing the work

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

- This project shows how alane (AlH_3) is an ideal hydride for the use (hydrogen liberation) end of the cycle. Except for ST-116 (Ardica Technologies [Ardica]), this is essentially the sole U.S. Department of Energy (DOE) project on this interesting and high-potential hydride. Alane is not reversible by direct rehydrogenation, so this project is correctly focused on electrochemical processes for efficient regeneration of spent alane (Al metal). The processes are complex and multi-stepped, but clearly possible. The many barriers are well addressed and are focused on DOE needs and targets for hydrogen storage for portable power fuel cells.
- This project is an interesting take on producing relevant amounts of alane by electrochemical means. The current process is extremely expensive and impractical for real applications. The team is addressing the inefficiencies by recycling materials, electrolyte regeneration, and reducing dendrite formation. It is a systematic line of work that is producing results.
- The project is aimed at relevant issues that are aligned to addressing barriers in order to meet cost targets. It is unclear from the presentation how well designed the approach is since most of the results are presented as final improvements and there is no sense that a range of parameters or materials has been investigated in an effort to optimize performance.
- The electrochemical method for formation of alane is more efficient than the conventional chemical route currently adopted by Dow Chemical. While the electrochemical method has been demonstrated in the laboratories, many practical issues remain for large-scale production. This project has encountered some of these issues (such as dendrite formation and crystallization of alpha-alane) and is still in the process of addressing them satisfactorily. Regeneration of $LiAlH_4$ is crucial in the overall scheme for using alane as a hydrogen storage material. However, there is no new information to address the low regeneration efficiency that was presented by the project in previous years. The assumption that $LiAlH_4$ can be regenerated in situ is highly questionable in practice. In all likelihood, $LiAH_4$ must be regenerated out of cell in a separate regeneration process.
- The approach is barely adequate and perhaps could have been improved with more integration and communication with the partner, Ardica. There was little experimental design considering that much of what the project is trying to accomplish is to make incremental improvements toward a viable process. This should be a systematic progression, but that was not apparent. There was little discussion of what the rates

of the various processes must be to make alane cost-effectively. The approach seemed to duplicate some of Ardica's approach, but in general, the project executed those areas of duplication at a much lower level, e.g., cost analysis. Perhaps a more thoughtful division of labor would provide DOE with a better set of projects. There were many typos in the slides, which seems to represent a lack of attention to program execution. The photographs of the chemical reaction glassware indicated a very sloppy-looking laboratory. This does not lend a feeling of confidence in the overall research and development efforts.

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

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

- Further progress in efficient alane synthesis and crystallization has been made. These are more evolutionary than ground-breaking but are nevertheless valuable.
- There is good progress in the recovery of additives, identification and control of the phases of alane, electrolyte material selection, etc. The project barriers are addressed one at a time.
- Impressive progress toward goals has been made on many fronts during this reporting period: dendrite elimination with a new MgNi electrode, recovery and recycling of reactants, better adducts, improvement of efficiency (suggesting lower alane ultimate production cost), improvement, and stabilization of the resultant AlH_3 crystalline product, to mention the main results. Importantly, the effort has resulted in the synthesis of excellent AlH_3 (98% of theoretical H-capacity). This long-standing project switched from onboard light vehicle to portable power targets in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRDDP), apparently because of high projected cost ($100/kg target). However, the Ardica companion project (ST-116) is currently projecting the possibility of significantly lower ultimate cost.
- An MgNiHx-based cathode was developed and implemented to reduce dendrite formation. It is unclear how pure LiH can be recovered from the electrode; this has yet to be proven. There are simple mechanical methods to solve the dendrite growth problem, such as using scrapers to scrape off dendrites and collect them in a basket underneath the cathode. This method has been successfully adopted in large-scale electrorefiners for reprocessing of spent nuclear fuel.
- This project's progress was not at the level expected. There was not much to report relative to last year. Perhaps it was just the presentation style that did not adequately reflect the true level of accomplishment. The most noteworthy accomplishment was the use of MgNi as a cathode material that seems to reduce dendrite formation. There was apparently little discussion of this development with the project partner, who is most concerned with developing an economically viable process, so it is not clear whether the Savannah River National Laboratory (SRNL) accomplishment can lead to improvements in the overall cost. Many of the highlights discussed by SRNL came from Ardica (and were properly attributed), but this seemed to indicate that not much new was happening on the SRNL end of the project.

Question 3: Collaboration and coordination with other institutions

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

- This project has good collaboration with partners Ardica and SRI International (SRI) but does not have any collaboration with other institutions outside of the partnerships with Ardica and SRI.
- There are excellent connections between the teams at SRNL, SRI, and Ardica. The project has an industrial component that is working in overcoming the barriers and making the process scalable.
- There are collaborations with cooperative research and development agreement (CRADA) partners Ardica and SRI, but the roles of these partners are not defined completely, especially that of SRI.
- Despite the frequent contact between the primary collaborators (Ardica) on this project, the evidence for the impact of this is not great. For example, the partners are independently using different adducts to replace tetrahydrofuran (THF) for crystallization without apparent reference to each other. The division of labor in some tasks is also not clear; both mention electrolyte recovery and developing efficient crystallization, for example, with no explanation of what role each is taking.

- The project's communication with Ardica appeared to be at less than nominal level. It appeared that results were not shared in a timely fashion (e.g., the MgNi cathode results were not discussed or mentioned by Ardica in the Ardica presentation). The SRNL "cost analysis" was too rudimentary to provide any useful technical guidance relative to Ardica's very comprehensive process/cost analysis.

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

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

- The project is very relevant to the portable power goals and objectives of the MYRDDP. Third parties are already interested in specialized applications of alane made by the synthesis process developed at SRNL.
- The project has potential to meet DOE goals in some portable power applications. Alane has sufficient hydrogen capacity, and the project is aimed at improving efficiency and reducing cost.
- The relevance is good, aligning with DOE objectives. The impact of this project is reduced, however, by the reduced level of accomplishment relative to prior years, and the SRNL work contains some duplication of effort with Ardica.
- The potential impact is limited because the material is unlikely to be low-cost. It may find niche applications in defense, long-term emergency energy storage, etc. However, it may get people to think of alternate and more "chemically sound alternatives" to store hydrogen in systems (unlike ball milling, for example).
- The cost to produce alane under the electrochemical method remains out of reach for light-duty automotive applications. Suitable applications could include portable low-power systems that use alane as a hydrogen storage material.

Question 5: Proposed future work

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

- The team has a clear and systematic line of work that so far has produced a real physical material.
- The future work proposed extends the project in the current direction and is somewhat general. It is not clear what is proposed for efficient recrystallization methods. Two of the bullet points relate to improving electrolyte conductivity (the first appears to have been completed this year). It would be good to establish a target for conductivity, perhaps using Ardica's cost and process models.
- The proposed future work is sound, aiming to improve cell conductivity by using THF and establishing a method to recover alane from the alane–THF adduct. There is no mention of work related to regeneration of $LiAlH_4$, which needs to be proven beyond small laboratory-scale and with high efficiency.
- Much of the future work in optimization could be better accomplished at Ardica, where the process details may come closer to realization. It was unclear whether the SRNL future work was in concert with what the project partner requires. The SRNL future work slides appeared unfocused and possibly with too many potential areas relative to the level of effort that can be applied.
- The remaining challenges and future work (slides 19 and 20) seem reasonable but rather open-ended. This project has no go/no-go decision point and is not very clear as to when there will be an end point. It can be argued that the project has made enough excellent basic progress that it can soon be ended and turned over to industry (Ardica) for practical cost optimization and commercial production.

Project strengths:

- The project is aimed at improving cost and efficiency of a relatively high-gravimetric-capacity material, and therefore is aligned with DOE goals.
- The principal investigator and his team have many years of experience working on this project, and their expertise is unique in the United States.
- A potential strength lies in the national laboratory–small company collaboration toward developing a viable commercial storage "product."

- This project is done in a systematic way and shows progress in an area that is, at the moment, stalled (hydrogen storage). Electrochemistry can be turned into an industrial process.
- The project is a very detailed attempt to make practical the low-cost production and use of a most interesting hydride, AlH_3. The approaches are innovative and practical.

Project weaknesses:

- The project is nearly complete and will soon get to the point of diminishing returns. The low-cost production/regeneration of alane is a significant challenge relative to the needs for light vehicle onboard hydrogen storage.
- The project does not show great structure and planning in overcoming barriers. The principal investigator's response to a similar comment from last year's review contains statements that are in general admirable but do not really address the comment. The project comes across in the presentation as a series of ad hoc experiments. Perhaps this is not the best way to make progress in this project. Communication with partners is good, but the outcome of this is not strong, and there appears to be duplication, and opportunities have been missed for this project to have goals more clearly set by Ardica's needs.
- Improving cell current and yield by using more a conductive agent such as THF brings along a different set of problems, as the alane–THF adduct is very stable. The transamination process with triethylamine to separate alane from the adduct is energy intensive and inevitably reduces the overall alane recovery efficiency.
- The material, alane, is unlikely to meet the demands for transportation, so its impact is reduced.
- The project as presented appeared unfocused. The project has a duplicative effort with partner Ardica and an apparent lack of significant progress relative to prior years.

Recommendations for additions/deletions to project scope:

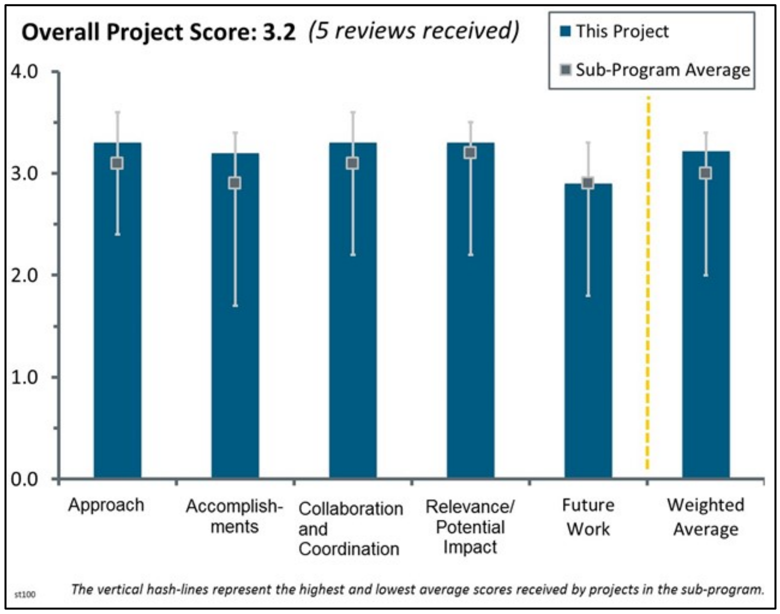
- This project is on track.
- The team should have a comprehensive meeting with partner Ardica to discuss where Ardica feels there are gaps, and then where SRNL can play a role in filling these gaps to move alane along the commercial pathway, if there is one. If there are gaps, then there should be a very detailed experimental design to optimize, make incremental improvements, etc., where the commercial partner believes there is the greatest need(s).
- This project would benefit from a reasonable go/no-go decision point and a plan to finish the remaining process details and turn the alane effort over to industry.
- The project needs a more coordinated approach with partners, with each concentrating on facets they can deliver to help one another.
- The project should include regeneration in future work and aim to achieve high regeneration efficiency.

Project #ST-100: Hydrogen Storage Cost Analysis

Brian James; Strategic Analysis, Inc.

Brief Summary of Project:

The goals of this project are to (1) conduct independent Design for Manufacture and Assembly (DFMA) cost analysis for multiple onboard hydrogen storage systems, (2) assess/evaluate cost-reduction strategies, and (3) identify pathways to reduce the cost of onboard hydrogen storage systems by 15% compared to the U.S. Department of Energy's (DOE's) 2013 record and meet the DOE 2017 target of $12/kWh for onboard hydrogen storage for light-duty fuel cell electric vehicles (FCEVs).



Question 1: Approach to performing the work

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

- With the specific objective of assessing factors that affect 700 bar Type IV hydrogen storage, the Strategic Analysis, Inc., (SA) team has provided a comprehensive evaluation that was expanded and updated to address issues raised during the 2015 review. They examined variations in carbon fiber (CF) materials and processing as well as balance-of-plant (BOP) components.
- The approach, including the uncertainty analysis for tank manufacturing, captures the improvements across the Hydrogen Storage program, and the DFMA analysis for the BOP components is very thorough and seems to be a very accurate reflection of what the costs could be after including the selling, general, and administrative expenses. It would be good to see this applied to some of the more quickly developing areas of the Hydrogen Storage program, such as the more promising materials. In the program manager's overview presentation, he highlighted alane several times, but there has not been a thorough cost analysis of alane by SA in the past several years. This would be very beneficial to the community, especially when attempting to drive the cost of this material to below $10/kg of alane.
- The project has a good approach.
- The approach is generally good, but in looking at manufacturing considerations, particularly winding time, there are a number of variables not considered to date. For example, winding with larger tows potentially appears to reduce winding time, but winding equipment does not generally handle very large tows well. Additionally, when considering lower-cost CF—even those that are currently commercially available—the nature of the material itself must be considered. While the material itself may be substantially lower in cost, significant tow breakage and "fuzzing" is observed in winding, resulting in a need to stop the process frequently to clean the winding apparatus and thereby increasing winding time. It is not clear whether there is actually a cost benefit to using lower-cost fibers.
- The cost focus is narrower than ST-001 but goes into more depth on compressed gas storage composite tank cost drivers. It would also be beneficial to see analysis on the original equipment manufacturer selection process to examine cost versus other design considerations, such as weight and volume.

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 updates to the modeling, including the uncertainty analysis to capture the research and development (R&D) advancements into the model, were great improvements and accomplishments for this group. Also, the focus on the alternative manufacturing techniques is very useful to the R&D and manufacturing community, considering the batch-style process that occurs for tank manufacturing currently.
- The project offers in-depth analysis comparing to the current 2013 benchmark—a good means for vetting potential cost-reducing concepts.
- The reported cost analysis for several relevant processes and tank components would help in reducing the high-pressure tank cost.
- The project provides guidance as to what potential methods of cost savings should be targeted for further R&D. However, that said, there are many nuances to the manufacturing operations—especially filament winding—that have not been addressed. The "fuzzing" issues with low-cost fibers are among these. Also, while some cost savings were realized with the vinyl ester resin systems for 700 bar Type IV systems, it should be understood that these systems may not translate as well into future work (e.g., cryo-compressed).
- After completion of its assessments during the current year, the SA team reported that less than a 15% net cost reduction could be achieved between the 2013 and 2015 status. While these newer values may be more robust than previously reported, they still are >40% higher than the 2020 cost targets. There seems to be little more to be gained from continuing these analyses at this time. There is also a major gap in extrapolating manufacturing and processing costs for less than 10,000 storage units per year to the case example for 500,000 units per year.

Question 3: Collaboration and coordination with other institutions

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

- The interactions and data exchanges between SA and its partners and other organizations seem strong and fruitful. There seem to be no issues in this area.
- The project offers a comprehensive team with strong ties to related projects.
- It seemed that a more concerted effort to collect data from other DOE projects was undertaken during this performance period.
- Collaboration is visible with other institutes and industrial partners.
- The interplay between Argonne National Laboratory and SA has seemed to work well. It is not clear how much the National Renewable Energy Laboratory is involved and what its exact role is in this project.

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

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

- The techno-economic analysis is a very important aspect that should guide DOE's direction in determining portfolio selection. This is also why it is important to have a broader outlook than just tank manufacturing, especially when the materials and systems are in such an early stage, but this is a key component to driving a great portfolio that definitely should continue.
- The merit of this project has been to provide an independent assessment of all the cost factors for large-scale manufacturing of hydrogen storage systems. Nearly all effort during the past year has been on the Type IV 700 bar compressed gas system, which is the only current contender for hydrogen FCEVs.
- The relevance toward reducing cost in 700 bar Type IV hydrogen storage systems is excellent. A cautionary note is, however, that analyses conducted here may not be entirely applicable to other up-and-coming storage concepts (e.g., cryo-compressed employing composite overwrapped pressure vessels). In these cases, other factors will need to be addressed.

- The project offers strong guidance to sort through various cost-reduction approaches.
- The cost analysis would help capture possible cost-reduction opportunities.

Question 5: Proposed future work

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

- The planned work is good; however, the project should include BOP and tank estimates for other ongoing projects. For example, the project should evaluate the effect of changing the Ni content in stainless steel on the cost (from ST-113) and the effect of material cost on the high-pressure metal hydride hybrid tank.
- The future work should take a broader view of the portfolio and definitely include a focus on the materials that are currently viewed as functional for the various applications (portable power, materials handling equipment, and vehicles), as these are all key sectors that can drive gross domestic product (GDP) and greenhouse gas reduction.
- The project should consider basalt fiber as midway between glass fiber and CF in performance and cost. The project should also consider economic drivers in cost versus performance, i.e., what drives the “buy” decision. It is not clear what the key material characteristics are that drive tank design; the project should consider thermal plastics or thermoplastic polyurethane (TPU) for tougher resins that may provide enhanced safety and damage tolerance.
- Since the updated comprehensive assessments of the Type IV tanks show little potential for any significant progress toward meeting DOE targets within the foreseeable future, SA appears to have taken its evaluations to a stopping point. There is little value in performing further analyses on this system, such as those listed on slide 24, beyond the end of fiscal year (FY) 2016.

Project strengths:

- The results produced by the SA team seem robust and well vetted as practical, considering the still very limited manufacturing production levels for FCEVs. Good collaborations with component developers and manufacturers should lead to more reliable results.
- The project has a very good approach, and the project has been progressing well.
- The project takes a comprehensive look at all aspects of 700 bar Type IV hydrogen storage vessels.
- The model has a strong basis but can add other features such as certification costs and tank finishing/rework, as well as scrap costs.

Project weaknesses:

- In order to reduce costs for BOP components of Type IV storage systems, the SA team has proposed highly integrated multi-function devices. However, the ability to manufacture such systems and validate their robustness and reliability remains to be demonstrated. Also, there seems to be little room to reduce cost for high-strength CF to the level necessary to reduce system mass and volume.
- The manufacturing assumptions remain a bit simplistic—more data from using low cost CF and towpreg should be collected to refine assumptions.
- There are challenges associated with predicting the effect of changing processes on the tank cost.
- The project should consider economic drivers in cost versus performance, i.e., what drives the “buy” decision. It is not clear what key material characteristics drive tank design; the project should consider thermal plastics or TPU for tougher resins that may provide enhanced safety and damage tolerance.

Recommendations for additions/deletions to project scope:

- It is recommended that the project include BOP and tank estimates for other ongoing projects. For example, the project should evaluate the effect of changing the Ni content in the stainless steel on the cost (from ST-113) and the effect of material cost on the high-pressure metal hydride hybrid tank (from ST-001).
- The project should consider economic drivers in cost versus performance, i.e., what drives the “buy” decision. It is not clear what key material characteristics drive tank design; the project should consider thermal plastics or TPU for tougher resins that may provide enhanced safety and damage tolerance.

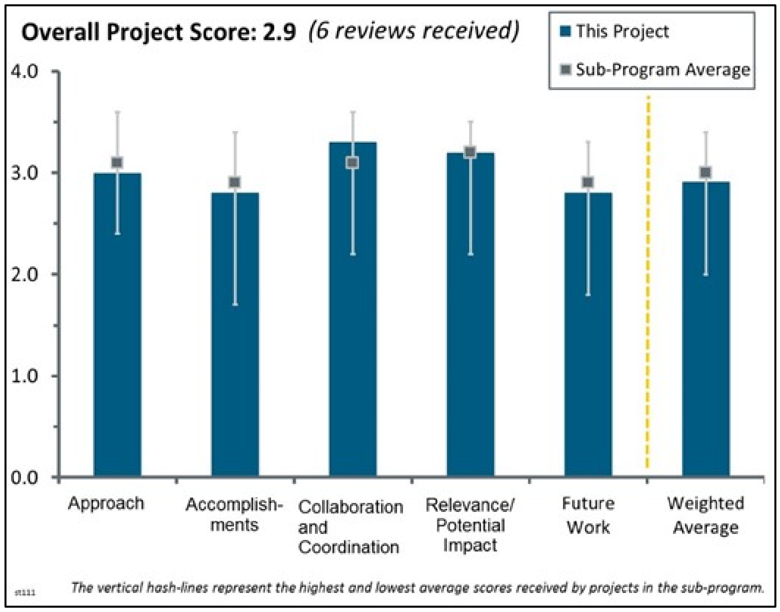
- In light of the current status of the competent analyses performed by SA and the lack of eminent improvement in carbon materials or BOP components, this project should finish at the end of FY 2016. The DOE resources could then be made available to investigate and develop higher-performing materials and improved components.

Project #ST-111: Thermomechanical Cycling of Thin-Liner, High-Fiber-Fraction Cryogenic Pressure Vessels Rapidly Refueled by Liquid Hydrogen Pump to 700 bar

Salvador Aceves; Lawrence Livermore National Laboratory

Brief Summary of Project:

The objective of this project is to demonstrate a scalable 700 bar cryo-compressed hydrogen storage system that storages 5 kg of hydrogen and is capable of achieving gravimetric and volumetric capacities of 9+ wt.% and 50 g/L, respectively. This system offers the potential to exceed the U.S. Department of Energy's (DOE's) weight and volume targets at a modest cost. In addition, a liquid hydrogen pump that can rapidly and consistently refuel cryogenic onboard hydrogen storage to 700 bar will be assessed.



Question 1: Approach to performing the work

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

- This continuation of several prior Lawrence Livermore National Laboratory (LLNL) projects on the development and demonstration of cryogenic compressed hydrogen addresses experimentally most of the critical issues concerning this high-capacity storage system. For widespread usage of onboard vehicles, robustness, safety, and durability of the Type III tank must be demonstrated during operation, and extended pressure–temperature cycling for this method must be considered.
- The facility is excellent and provides a national capability for testing hydrogen storage tanks. The one flaw is that it has very little instrumentation to detect onset of tank damage such as acoustic emission sensing or in situ nondestructive evaluation (NDE).
- Both the approach to develop the testing facility and the approach toward the demonstration of cryogenic cycling are excellent. However, the broad scope of the project seems almost to interfere with making progress on the tank aspects of the work. The project should have been considered as two projects.
- The goal of this project is to develop and demonstrate a cost-effective 5 kg cryogenic hydrogen system at 700 bar with 9+ wt.% and 50 g/L. The stated approach is to test the durability of four 65 L prototype vessels before building a 5 kg 700 bar cryo-compressed hydrogen system demonstrating 50 g hydrogen per liter. Phase 1 objectives (instrumentation to measure cryo-pump power and boil-off, a safety plan for a cryogenic hydrogen cycling facility, and a 1600 bar cryogenic liquid nitrogen [LN2] strength test of an initial prototype design) have been accomplished. Phase 2 objectives (a containment system for 1300 bar 160 K hydrogen burst and 700 bar cycling to 300 K) have been partially accomplished. Phase 2 objectives yet to be accomplished are 1500 cycles and cryogenic hydrogen end-of-life strength testing of two vessels. Phase 3 objectives that will be done subsequently include aggressive cycling and then strength testing of two higher-performance vessels, installing the final vessel design in a lightweight compact vacuum jacket, and performance demonstration (volume, peak hydrogen density, dormancy, and vacuum stability). However, slide 19 indicates that many of these Phase 3 objectives may need to be renegotiated. This greatly lowers the confidence that this project will be successfully completed. The approach is focused on developing and demonstrating a viable tank that can withstand 700 bar. Much care has been paid to safety aspects of the containment system and the liquid hydrogen (LH2) pumping apparatus. However, not enough attention has been paid to topics such as hydrogen boil-off and overall economics of the

technology. Slide 22 very briefly touches upon driving range inconsistency due to cryogenic refueling, but the corresponding inevitable boil-off when periods of frequent use are intermingled with periods of infrequent use has not been addressed. The thermal insulation aspects have also not been adequately addressed.

- The approach of this project is too aggressive, as it attempts to develop cryo-compression for both high-pressure and cryogenic temperatures. The advantage of decreasing the temperature is to reduce the pressure. The project should have considered the optimization of the pressure vessel at a lower pressure rather than 700 bar. In addition, the project should have avoided welding for liner construction and considered current seamless tank liner technology. The project should also have included an evaluation of the thermal insulation.
- The approach for this project was too ambitious and reflected poor planning from both the principal investigator (PI) and DOE. It is not certain what value will be gained from the sum total of the project because of the approach. A better approach would have been to focus first on a facility that could perform the testing, then develop individual components (e.g., identify a liner material, cycle it, do vacuum insulation, cycle it), then develop a system from these and demonstrate that through performance cycle testing.

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 completion of construction and successful commission of the LH2 pump that permits filling cryogenic vessels with cryogenic hydrogen at 700+ bar is a significant accomplishment. The difficulties of manufacturing the Type III pressure vessel that satisfies safety criteria have certainly had an impact on the proposed schedules for subsequent full-scale fueling and cycling tests. However, the team needs to address the production and qualification steps to fabricate vessels that can pass the inspections. On the other hand, confirming that both the LH2 pump and cryogenic pressure vessel satisfy operation and life cycle criteria is necessary for this project to reach its stated objectives.
- The project has made excellent progress building and testing the facility. There is more to be done for in situ monitoring.
- While Phase 1 and some Phase 2 objectives have been accomplished, significant and challenging Phase 3 tasks are yet to be performed. The one major accomplishment has been to build the containment system for LH2 cycling tests. On the tank side, the project demonstrated an LN2 tank to 1560 bar burst pressure. However, all subsequent tests with water cycling up to 700 bar fell short of the project's stated metrics. The project was unable to achieve the desired results with ambient temperature water cycling, which was attributed to manufacturing deficiencies (lack of roundness and poor weld quality). The team's solution to inadequate ambient water cycling performance is to proceed immediately to LH2 cycling with the belief that cryogenic temperatures will improve elastic range, ultimate stress, and fiber modulus and, hence, cycle life. This feels a bit like throwing a "Hail Mary" pass. A more prudent approach would be to address and eliminate the manufacturing defects (lack of roundness, poor welds), retest with water, and only then proceed to LH2. Thermal stability and the inevitable boil-off have not been addressed. Overall, the project seems to be in some jeopardy. The accomplishments to date do not create a feeling of confidence that the remaining tasks will be successfully completed.
- Good progress has been made on the hydrogen test facility, considering all of the hurdles that needed to be overcome. In retrospect, siting the facility in a location without the seismic code requirements might have allowed this aspect to proceed faster. There seem to be many issues with the thin liner—many failures during autofrettage and at relatively low cycle numbers. It is not clear what specifically is being done to address the issues with the liner. At this point, the high-pressure target seems completely unrealistic. There may be value in determining exactly how high you *can* go; this information could provide guidance toward system improvement. Also, additional NDE sensors during testing would be useful. It is not certain that they really *need* to be hydrogen-rated. The project could consider stopping a test as soon as a leak is detected and flushing the system with nitrogen to prevent hydrogen contact with air.
- The accomplishments thus far have been mainly related to station certification, which is a tremendous accomplishment but only a small part of achieving the project goal. The failures in developing the tanks

and liner materials so far are learning opportunities, and it seems that the investigators are progressing, just not at the expected schedule required to complete this project. This reflects poor planning.
- The project accomplishments were minimal since the tank designs were unable to achieve the desired cycle life, even at room temperature and during autofrettage. The project has accomplished the construction of the test facility, although this facility was not required for identifying the failures with the tanks since the issues occurred at room temperature.

Question 3: Collaboration and coordination with other institutions

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

- Partners include Linde, BMW, and Spencer Composites. The responsibilities of the team members are well defined, and the team seems to be working well together.
- There appears to be very strong long-term and close collaborative interactions among the LLNL, Linde, and BMW partners providing complementary expertise to this project. The pressure vessel fabricator (Spencer Composites) seems to have appropriate experience, although meeting the properties for cryogenic and 700+ bar pressures may be a greater challenge than initially assumed. It does not appear that this team has contacted other organizations (e.g., NASA laboratories or contractors) that also have extensive high-pressure and cryogenic hydrogen expertise.
- The project's collaboration with industry leaders with cryogenic hydrogen is excellent, although the tank supplier may not be the appropriate partner for the tank design. The tank development for this project should not have experienced premature issues in autofrettage and room-temperature cycles.
- Collaboration between other institutions and LLNL seems to be adequate. It is not clear whether there is any direct communication between BMW and Spencer or if it is all done via LLNL as the middle man. There could be significant benefit in direct contact.
- The collaboration between LLNL, BMW, Spencer Composites, and Linde seems to be adequate to complete the project. Additional consulting on the liner failure issues might be required.
- Collaboration needs to include expertise for structural health monitoring and NDE. The project will have much more value if progressive damage can be monitored to help understand failure mechanisms.

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

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

- This is a unique project within the DOE Fuel Cell Technologies Office (FCTO) portfolio on the development of appropriately sized and efficient cryogenic hydrogen storage. This project will provide the only empirical data necessary to assess whether this concept actually provides for increased operating range over a broad spectrum of vehicle classes.
- The relevance of this project is highly aligned with the DOE research, development, and demonstration goals, as the project attempts to achieve a system with 9+ wt.% and a volumetric density of 50 g/L. Previously, cryo-compressed hydrogen was projected to have the potential of meeting the 2020 DOE system targets. It is important to have this project in the portfolio to evaluate and develop this technology.
- The project has great potential for Hydrogen Storage program impact if sensors to monitor tank failure onset are included.
- Hydrogen storage is a very challenging problem from a technical and economic point of view. To commercialize fuel cell vehicles, developing a viable solution to this problem is essential. Hence, this project is well aligned with the Hydrogen and Fuel Cells Program. However, the main concern is this: even if this type of pressure vessel were successfully demonstrated within the scope of this project, major questions pertaining to safety (inevitable boil-off) and economics (whether the LH2 approach is really viable from a well-to-wheels perspective) remain unanswered.
- The relevance of the project is good in that the cycling of thin-lined vessels for cryo-compressed storage needs to be understood. It is assumed that liner embrittlement upon long-term exposure to hydrogen has

been considered in designs, but this is not clear at this point in the project. Since no real cryogenic cycling with hydrogen has been conducted to date, it is difficult to assess the value of the data at this time.
- Cryo-compressed vessels could have a significant impact on a vehicle's storage capacity and volumetric efficiency, but there could be significant trade-offs because of hydrogen boil-off related to driving patterns that might force these vessels into niche applications that are not applicable to light-duty vehicles.

Question 5: Proposed future work

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

- Future proposed work is excellent but relies heavily on success with thin-lined vessels in cryogenic hydrogen cycling to high pressures. At this point, there is no convincing evidence that this goal will be met, placing the longer-term objectives in jeopardy.
- The team needs to focus primarily on the fabrication and qualification procedures for producing cryogenic Type III storage vessels with the "conservative design" 1.5 mm metal inner wall. Safety and durability are much more important to establish than slightly larger storage capacities at this stage. Optimization can occur during later development. However, increasing dormancy and providing robust thermal isolation are important issues that need to be addressed.
- Phase 2 objectives yet to be accomplished are 1500 refueling and cryogenic hydrogen end-of-life strength testing of two vessels. Phase 3 objectives listed include aggressive cycling and then strength testing two higher-performance vessels; installing the final vessel design in a lightweight compact vacuum jacket; and performance demonstration (volume, peak hydrogen density, dormancy, and vacuum stability). Slide 19 indicates that many of these Phase 3 objectives may need to be renegotiated. This greatly lowers the confidence that this project will be successfully completed. Overall, the project seems to be in some jeopardy. The accomplishments to date do not create a feeling of confidence that the remaining tasks will be successfully completed.
- The proposed future work does not include specific steps to resolve the root causes of the premature failures or a change in direction to ensure the project can demonstrate cryogenic hydrogen cycling. The effort needs to be redirected toward lower pressures and/or seamless liner constructions.
- The proposed future status of this project is sketchy at best, considering that the team has not achieved a successful tank design. The investigators admit that it will require renegotiation of current milestones and go/no-go to achieve success, which reflects poor planning on the part of both the PI and DOE.
- Tanks should not be tested until proper NDE and structural health monitoring (SHM) are in place.

Project strengths:

- A unique cryogenic hydrogen filling station has been assembled at LLNL, and a comprehensive safety evaluation has been completed. This is certainly the best location in the United States to evaluate directly the behavior of charging and discharging cryo-compressed hydrogen storage vessels.
- The development of the containment system is a project strength. The hope is that the containment system developed at considerable expense will be available for use by other parties. Whether this project will reach a successful conclusion is questionable.
- The project's strength is the development and optimization of cryo-compressed technology, which could have near-term potential to be competitive with 700 bar compressed storage systems.
- The project addresses key issues with hydrogen refueling for the case of cryo-compressed storage.
- The project has excellent test facility capability.

Project weaknesses:

- There have been many liner failures during autofrettage and leaks occurring at very low cycling levels. It is not evident that there is a clear and concise plan to address these issues, which appear to be at the welds. It is not clear what exactly is being done to address these failures, whether different joining methods or relocation of the welds from the dome to the cylindrical section, etc. At the present time, the capabilities of these cylinders are unknown. They are supposed to be for 700 bar storage, but it is not clear what the maximum operating pressure *really* is at this point. It could be 350 bar, 500 bar, etc.

- Although considerable funding is allocated to this work compared to most FCTO projects, the costs for fabrication, enhanced inspection and qualifications, testing, and cycling are quite high. From leak and burst behavior of the first six pressure vessels, more effort probably will be necessary that affects not only schedules but also budgets.
- The weakness of the project is the aggressive approach for high pressure and cryogenic temperatures while attempting to optimize the tank construction. The project would have benefitted from a systematic incremental approach rather than reaching and failing to achieve the maximum bookend.
- The design and development of Type III cryo tanks at 700 bar have faced some technical hurdles to date. It is not clear whether these hurdles can be successfully overcome.
- Tanks should not be tested until proper NDE and SHM are in place.

Recommendations for additions/deletions to project scope:

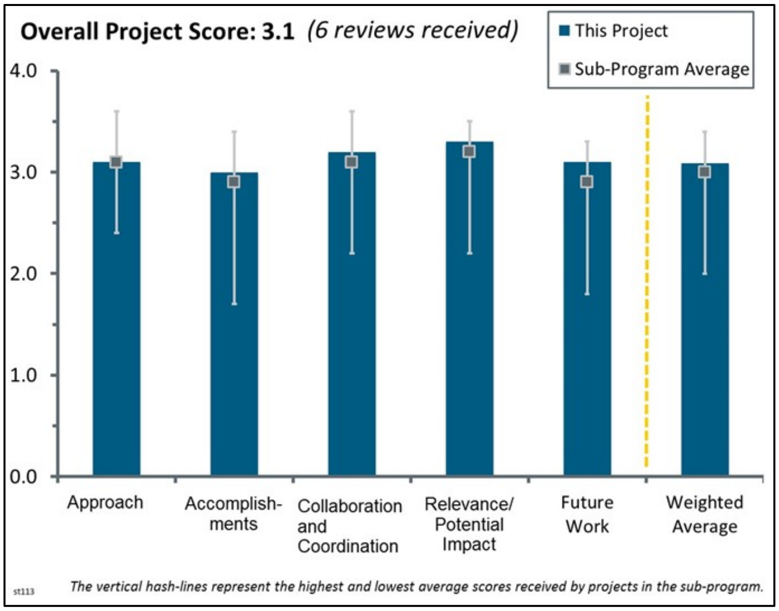
- The PI has indicated a second go/no-go: a successful cryogenic 1300 bar (SF = 1.85) strength test of at least one prototype vessel after 1,000 thermomechanical cycles. This is a reasonable approach for the continuation of the project. However, it would also be good to see the project demonstrate a successful water cycling test after addressing the manufacturing deficiencies (roundness, welding quality). During the question-and-answer session, it was suggested that NDE methods be employed to detect cracks and other defects in tanks. This will save time and costs compared to cutting open the tank and examining it visually. It was also suggested that welds should be eliminated completely rather than trying to get good welds.
- First, more prototype Type III pressure vessels should be fabricated and validated via several testing methods with both hydraulic and hydrogen gas pressurizations prior to initiating the extended cycling work. Also, more qualification measurements are needed on assembled components using NDE and cryogenic proof testing, along with the future testing proposed on slide 23. It is strongly recommended that LLNL contact appropriate NASA hydrogen expert personnel for some advice and possible support.
- The recommendations for this project scope are to focus on lower pressures, seamless liners, an alternative tank supplier, and an incremental understanding of the cryo-compressed tank design. In addition, the project's cycle criterion is too low at only 1500 cycles. The lower cycles are fine for initial screening, but there should be a fatigue projection for the industry standard in the Global Technical Regulation for 5,500 cycles. A cost projection of the technology would also be useful for comparison to the 700 bar technology.
- Inner cylinder performance goals should be met before proceeding with any work on the insulation/vacuum jacket.
- Tanks should not be tested until proper NDE and SHM are in place.

Project #ST-113: Innovative Development, Selection, and Testing to Reduce Cost and Weight of Materials for Balance-of-Plant Components

Jon Zimmerman; Sandia National Laboratories

Brief Summary of Project:

The overall objective of this project is to identify an alternative to high-cost metals for high-pressure balance-of-plant (BOP) components. The project goals are to (1) reduce weight by 50%, (2) reduce cost by 35%, and (3) expand the scope of construction materials for BOP.



Question 1: Approach to performing the work

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

- This project aims at U.S. Department of Energy (DOE) cost and weight barriers by looking to reduce BOP components of austenitic stainless steels through composition changes (i.e., metallurgical modifications, particularly lower Ni contents than Type 316L conservatively used austenitic stainless steel). In particular, the tensile and fatigue strengths of alloys are being measured in hydrogen. This approach has not been systematically explored of late and is needed to address DOE cost and safety barriers. The project is well designed. The attempts to calculate and measure stacking-fault-energy with fatigue and strength properties in hydrogen should result in important new fundamental metallurgical understandings of hydrogen embrittlement. However, there should not be overreliance on stacking fault energy (SFE) alone. Limiting the main composition variable mostly to Ni is probably too restrictive, i.e., Cr is another important composition variable. The project targets (-50% weight and -35% cost go/no-go) are very quantitative, ambitious, and directed at important DOE barriers.
- Combining density functional theory (DFT) with experimental efforts to understand the material properties of steels and other BOP types of materials and predict and measure advanced materials is an adequate approach. However, it seems this project has gotten off to a slow start with some of the fiscal year 2015 milestones still not 100% completed. The theory associating SFE with material stability is a reasonable approach and should be able to be adequately described in DFT space.
- The researchers are using a combination of theory and experiment, which can be a good approach. The targets, except the go/no-go, seem reasonable if the cost and mass reductions are for the BOP components only while maintaining material performance. The project is looking at some low-temperature testing (-50°C); however, cryogenic testing needs to be included.
- Reduction of the BOP costs through the use of alternative steel alloys is expected to substantially lower the tank’s system cost.
- The approach of the project attempts to combine both experimental and computational methods to evaluate the current 316L material and recommend alternative materials with lower Ni content. The fatigue performance assessment appears to be useful and a better method than the historical tensile data. It is unclear whether the computational efforts with the SFE will provide a useful outcome in recommending other materials for hydrogen applications.
- This project combines experiments and computation. In principle, this combination should accelerate the development of optimal materials. One concern is the feasibility of the DFT calculations, which have proven to be more complex than expected.

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.

- Many new and highly useful data have been generated in the last year. The project is moving along at a very useful rate toward accomplishing its objectives and DOE goals. It seems likely the project will pass the go/no-go decision point.
- The progress is good where failure testing and modeling of SFE have been conducted.
- The project seems to be making good progress with experimental measurements. The computational work has not made a significant contribution because of complications associated with calculating the SFE of complex magnetic alloys.
- The project has progressed, although further results were expected based on the extensive experience of Sandia National Laboratories (SNL) in this area of hydrogen embrittlement. The characterization of new materials is useful, but the project should also ensure the fatigue approach is developed into an acceptable screening method. SNL is also involved in a broad effort to progress the advancement of hydrogen embrittlement standards. This work should be indicated when discussing the progress of this project.
- The investigators have identified and started to demonstrate a reasonable testing method for assessing the fatigue life of materials in hydrogen. It would be imperative to extend this to both temperature and pressure ranges. It is recommended that the go/no-go be reassessed to enable discovery of a broader range of new materials to meet the performance and cost improvements.
- For the budget, more accomplishments would be expected. It is unclear how the experiments are validating the theory. The researchers say they are using scanning electron microscopy for this, but the connections need to be clarified. It is unclear how the theory is helping the progress, and it seems they are testing the same materials as last year.

Question 3: Collaboration and coordination with other institutions

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

- The collaborations are excellent, not only in the fatigue testing area (High-Performance Materials Testing) but also with a BOP manufacturer (Swagelok) and stainless steel manufacturer (Carpenter).
- Strong collaborations appear to exist with Swagelok, Carpenter, and Hy-Performance.
- The current collaborations with Hy-Performance, Swagelok, and Carpenter seem adequate if the project is going to move toward more of a development-of-materials stage. The investigators should reach out to other expertise within the national laboratory community, as there is a wealth of expertise on hydrogen exposure on steels and other materials in the NNSA laboratories, and the investigators are part of that community.
- The collaboration of the project is clear between the SNL experimentalist and theorist, although the contribution of the other partners is not well defined. It would be helpful to have further input from Swagelok and other manufacturers regarding the cost and machining of these materials. In addition, SNL should acknowledge other involvement with standards organizations and international organizations in the assessment of hydrogen embrittlement.
- The project shows that there is collaboration with other institutes and an industrial partner who is a BOP developer.
- The project has engaged materials companies and component suppliers, and this is a good team, but the interactions with the collaborators are unclear.

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

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

- The project clearly supports and advances progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan. The project adds much-needed BOP weight and cost support.
- The project provides an important area of study regarding evaluating the fundamentals of hydrogen embrittlement. The focus of the project is aligned with the DOE research, development, and demonstration goal to reduce the cost and weight for compressed hydrogen storage systems.
- The project's high-pressure tank's system cost can be reduced using alternative BOP components.
- This project is relevant because we need lower-cost, lighter-weight BOP components.
- The project shows how reducing the cost of BOP components is an important objective.
- The project could have a reasonable impact on hydrogen storage systems and tank components, but the reviewer is not totally convinced that the project will identify new materials.

Question 5: Proposed future work

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

- The future work provides good detail on the next steps to address the challenges of characterizing materials for hydrogen embrittlement. The future work should include a path to implement the outcome of the project in screening methods for other materials.
- The proposed future work for the remainder of the project is reasonable. It is important that the practical acceptances of Swagelok and Carpenter for the new alloy(s) be in place by the end of the project.
- The plan is good overall, but it would be useful to correlate the alloy composition to cost and performance so that trends are obtained.
- The go/no-go in this project seems very weak. From the simple analysis, it is clear there are several candidates to meet the cost and mass reduction. This should be changed to meet cost, mass, and performance requirements. As written in the presentation, the go/no-go does not have any performance requirements. Performance requirements need to be added to make the go/no-go meaningful; they need to validate the theoretical work. At this point, it is unclear what value the computational work is providing in the search for new materials.

Project strengths:

- This project is extremely well funded for the work scope.
- The project has appropriate collaboration and approach.
- This project has a sound metallurgical approach for lowering BOP weight and cost.
- The strength of the project is the fundamental understanding of hydrogen embrittlement and the pursuit of materials with low cost based on lower Ni content.

Project weaknesses:

- The project seems too focused on select types of steel alloys.
- The project needs some cryogenic testing, and how the experiments are used to validate the theoretical is not clear.
- The project does not have enough time to experimentally confirm all the effects and new alloys that are calculated to have potential.
- Given the configurational and magnetic complexity of these alloys, it is unclear whether the DFT calculations will make a meaningful contribution during the timeframe of this project.
- The project overestimates the BOP improvement for both cost and weight by replacing the 316L stainless steel material. Many components in the BOP utilize aluminum rather than 316L stainless steel, so the

improvement will be limited, and the new materials should be compared against aluminum. Also, the project needs to ensure that the new information is highlighted to distinguish it from previous SNL efforts in the area of hydrogen embrittlement.

Recommendations for additions/deletions to project scope:

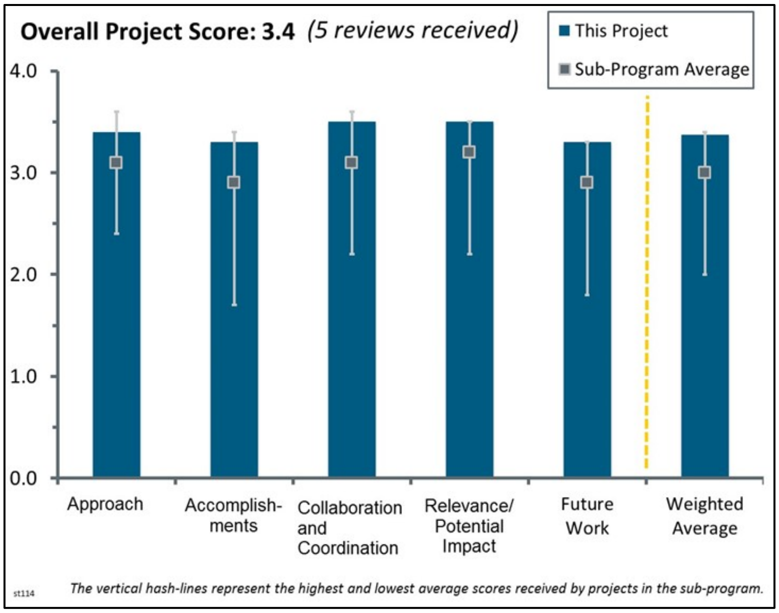
- In addition to exploring the magnetic contributions to the SFE, it is not obvious that configurational degrees of freedom have been considered. For example, if these alloys are solid solutions, then short-range order can lower the energy of the system compared to a truly random atomic arrangement. The project should also consider comparing reliability of the indirect estimates provided by the expression for SFE (slide 13) and direct calculations.
- The project should extend the studies to other cheaper steel alloys to make property/performance correlations. In addition, for best-performing alloys, it would be useful to take into account interfacial effects, i.e., oxides, etc., as these can affect the alloy performance.
- The team should consider Cr as a variable, in addition to Ni. Such an approach should be extended to nonferrous alloys (especially Al) in a follow-on project.
- The BOP improvement opportunities should be reconsidered based on actual BOP component designs. The project scope should also include a direct connection and acknowledgment of the opportunity to influence codes and standards related to hydrogen embrittlement based on the outcome of the project.
- The milestones of the project need to be revisited, especially the go/no-go.

Project #ST-114: Next-Generation Hydrogen Storage Vessels Enabled by Carbon Fiber Infusion with a Low-Viscosity, High-Toughness Resin System

Brian Edgecombe; Materia

Brief Summary of Project:

The objective of this project is to develop and demonstrate a 700 bar Type IV composite overwrapped pressure vessel (COPV) with (1) a reduction in carbon fiber (CF) composite volume of 35%; (2) a cost of composite materials of $6.5/kWh, which is an important element of the U.S. Department of Energy (DOE) 2017 system cost target of $12/kWh; and (3) performance maintained (burst strength of 1,575 bar and 90,000 cycle life).



Question 1: Approach to performing the work

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

- The approach of proving concepts using plate samples and then proving them out on small-scale prototypes is excellent. It has allowed a better understanding of void content effects on shear strength, which roughly correlates to burst strength. The project should continue to follow the same approach to resolve any issues with vacuum infiltration and then apply those learnings to larger prototype vessels.
- The idea of using a high-toughness, infusible resin offers many benefits to both tank fabrication and overall performance. The use of vacuum-based processing will greatly reduce the void content of the resulting composite.
- The project provides strong potential to reduce tank cost through better matrix, better quality, and faster winding.
- The overall goal of this project is to demonstrate a 700 bar Type III COPV with 35% reduction in CF composite volume to reduce the cost of composite materials to $6.5/kWh, while maintaining performance of burst strength of 1575 bar and 90,000 cycle life. The technical premise of this project is that the use of very low-viscosity resins (< 20 cP) during vacuum infusion of dry-wound forms will greatly reduce the incidence of voids (<1%), which can cause significant knockdowns of shear strength, which is important in the shoulder region of the tank. Additionally, the high fracture toughness of the Proxima resin is expected to contribute to better COPV performance. The overall proposed methodology for meeting these objectives, such as fabricating test plates with deliberately introduced voids via controlled air leaks and preparing and bursting small Type III COPV tanks, appears to be sound. The use of inspection methods such as void characterization, finite element modeling of the vacuum infusion process, and use of laser-based non-contact measurements of diameter changes associated with fiber crimping or buckling is reassuring.
- The approach of the project is to reduce voids with vacuum infusion, increase fatigue performance, and improve crack resistance. It is helpful to explore alternative manufacturing methods to the traditional wet winding, although the project could be improved in respect to confirming the relationship between voids and CF reduction opportunities. In addition, the cycle criterion for the project is too high. The certification standards are 11,250 cycles with a maximum number at 45,000 cycles rather than the 90,000 cycle target in the project.

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 following tasks have been completed: (1) demonstrate infusion process feasibility (thin and thick plates), (2) design a tank using models and materials data (static and fatigue), (3) conduct dynamic testing on composite plates, (4) prepare small tanks (Type III) as "proof of principle" for the process, and (5) design a COPV winding pattern for full-size Type IV tanks. The researchers have successfully demonstrated small Type III tanks to a burst pressure of >26,000 psi using their dry-wound vacuum infusion process. They have used laser scanning to characterize compaction of fibers during vacuum infusion and identified fixes to processes that cause localized compaction and buckling. They have conducted tension–tension cycling on glass fiber composite plates at 0.7% strain (corresponding to hoop strain at the maximum operating conditions), while deliberately introducing voids of a desired percentage via controlled air leaks. These laminates showed excellent retention of tensile strength despite moderate void content. Finally, they have completed an Abaqus flow model of the vacuum infusion process to aid experiments. All indications are that they are making strong progress toward meeting their goals.
- Significant accomplishments have been made and demonstrated with subscale tank production and testing. The reviewer has some concern about additional variables that will be introduced during the last few months of the project: (1) the switch from Type III to Type IV cylinders (should be mitigated by Spencer Composites participation), (2) the switch to Toray fibers from Mitsubishi (many factors can contribute to performance: handling during winding, fiber sizing effects on adhesion, and subsequent load transfer/fiber property translation), and (3) infusion at larger scale.
- The accomplishments during the past year to resolve void properties and winding/buckling issues by combining results from the modeling efforts have been impressive. The project seems to be progressing toward demonstrating the total process on larger-scale prototypes that will meet the DOE goals.
- Tanks were successfully fabricated and tested; quality was good (low voids).
- The accomplishment of manufacturing a tank with COPV infusion is good, although the results have not shown correlation to reducing the CF content. In fact, the cost analysis has shown an increase in cost from the baseline wet winding tank design.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration between Materia, Spencer Composites, Hypercomp Engineering for filament winding optimization, Montana State University (MSU) for finite element analysis (FEA) modeling and plate sample analysis, and Powertech Labs for full tank testing seems to be organized and coordinated effectively to achieve the project goals of cost savings.
- Materia seems to be taking advantage of expertise at partner institutions to quickly optimize processes involved in achieving the project goals.
- The collaboration seems to have clear responsibilities and roles. It was excellent to have the cost analysis performed by Strategic Analysis, Inc., in this year's effort. The project would benefit from having a series-production tank manufacturer either as a partner or in a consulting role to better guide the development toward commercialization.
- Partners include MSU for FEA modeling and mechanical testing; Spencer Composites for filament winding, fiber winding modeling, and burst testing; and Hypercomp Engineering and Powertech Labs for testing and modeling. The roles of MSU and Spencer Composites are clear; the roles of the other two partners are less clear.
- The project has a strong technical team. It is not clear whether Spencer Composites will commercialize the technology. It would be beneficial to see an original equipment manufacturer or compressed gas storage (CGS) converter on the team.

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

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

- The project clearly supports the goal of DOE's Hydrogen and Fuel Cell Program (the Program) toward making cost-effective and safe hydrogen storage systems.
- This project can really have an impact on the manner in which tanks are manufactured. The process could be more amenable to an assembly line production over traditional wet winding of tanks, and it could possibly reduce some of the uncertainty with voids created during the wet winding process that might reduce the cycling durability of the tanks. Ultimately, if the project can reach the goal of reducing the cost of tanks by 35% from the 2012 baseline cost, it will allow greater adoption of fuel cell technology.
- The project is well aligned with the Program goals of cost reduction and/or performance enhancement.
- The relevance is high for this project because it is attempting to reduce the cost of the main factor associated with the compressed hydrogen tank system, which is the CF. The objective to reduce the CF by 35% is a stretch for this technology, although it would be significant if achieved.
- The project has strong potential impact but needs to focus on winding speed considerably. The project may need to interact with a fiber supplier and sizing company to maximize winding speed. The project could have a possible follow-on through the Institute for Advanced Composites Manufacturing Innovation.

Question 5: Proposed future work

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

- The proposed future work was well in line with meeting the requirements to test small-scale prototypes for dry winding vacuum-infused vessels.
- Proposed future work is appropriate, but the project should add enhanced fiber sizing to maximize winding speed and perhaps enhance infusion time.
- The future work is fine, although additional detail could be provided to demonstrate the CF reduction. This project seems to be focused on developing the infusion manufacturing process rather than focusing on the composite volume reduction from the baseline tank.
- The major remaining technical challenge is the vacuum infusion of large (full-scale) prototype tanks. The principal investigator (PI) indicates that wet winding will be considered if vacuum infusion cannot be achieved. Unfortunately, reverting to wet winding will negate the primary technical premise of this proposal, which is that the use of vacuum infusion will reduce the formation of voids. There is considerable expertise in the composites community for vacuum assisted resin transfer molding (VARTM) processes for complicated geometries. It is a bit surprising that the PI is so willing to give up this major advantage of the team's proposed method without fully investigating avenues to pursue vacuum infusion to the fullest extent possible.

Project strengths:

- The project explores an innovative pathway to reducing cost and/or improving performance of COPV for high-pressure hydrogen storage. The project team is excellently structured to achieve maximum progress toward Program goals.
- A well-conceived project has been executed so far for reducing the cost of Type IV COPVs by using a vacuum infusion process to reduce the formation of voids and thereby reduce the amount of CF that has to be employed. The project has employed a good mix of modeling and experiments with panels and small-scale tanks to demonstrate feasibility. The team has also employed void characterization and laser scanning measurements to identify and mitigate fiber buckling and undesirable fiber compaction during the winding process.
- The novel approach to reduced CGS tank cost has potential to succeed and opens the door for novel resins and fibers.
- The project strength is the focus on the key cost driver for compressed hydrogen tanks.

Project weaknesses:

- If wet winding of the Proxima material is to be considered, it probably would have been advantageous to look at it earlier in the project. Resin viscosity and pot life requirements vary substantially between the two processes, and formulation adjustments and/or process changes to conventional wet winding may be necessary (and time-consuming). Difficulties may be encountered in changing from Mitsubishi to Toray fibers. No two fibers handle alike, and achieving the necessary degree of fiber property translation could be difficult. There is not much room to accommodate this within the budget/timeframe remaining.
- The team's readiness to revert to wet winding in the event that vacuum infusion proves intractable for the full-scale prototype tank is disconcerting. It is not clear why the team does not leverage the vast experience in the composites community with regard to VARTM processing and thereby fully accomplish its objective.
- The project needs to optimize fiber tow sizing to increase winding speed and needs to reduce waste from the resin infusion process by using state-of-the-art reusable materials.
- The project needs to emphasize the CF reduction potential of the technology and correlate the voids to improved performance. The models developed in the project should be further utilized to evaluate the potential of the technology.

Recommendations for additions/deletions to project scope:

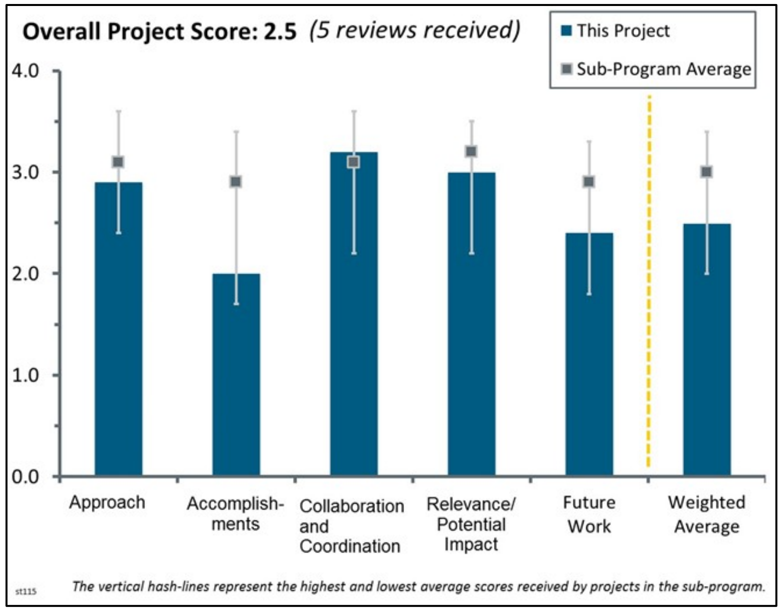
- The team should leverage the vast experience in the composites community with regard to VARTM processing and thereby fully accomplish its objective of vacuum infusing the full-scale prototype tank.
- The project needs to optimize fiber tow sizing to increase winding speed and also needs to reduce waste from the resin infusion process by using state-of-the-art reusable materials.
- The project scope should emphasize the demonstration of CF fiber reduction at appropriate cycle life rather than just proving the feasibility of the vacuum infusion process. The cycle life target should be reduced from 90,000 to the industry standard. Adding feedback with a series production tank supplier would help in formulating a commercial path and ensure other important parameters are not overlooked in the manufacturing development.

Project #ST-115: Achieving Hydrogen Storage Goals through High-Strength Fiberglass

Hong Li; PPG Industries, Inc.

Brief Summary of Project:

The objective of this project is to develop a Type IV composite overwrapped pressure vessel (COPV) reinforced exclusively with glass fiber having composite strength that matches T700 carbon fiber composite at less than half its cost. The project will also demonstrate a novel glass fiber manufacturing process and study the stress rupture behavior of composites made from the new fiber.



Question 1: Approach to performing the work

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

- The approach, by creating a high-strength glass fiber that could potentially meet or exceed the strength of Toray T700 carbon fiber, would substantially reduce the cost of hydrogen storage tanks for fuel cell electric vehicle applications. An analysis of the associated weight penalty and its effect on driving distance per fill-up would be interesting.
- The approach of preparing glass fiber with higher strength than T700 would help reduce the compressed tank cost.
- The approach, using low-cost, high-strength glass fiber, is of value.
- The goal of this project is to reduce composite contribution to the cost of Type IV COPVs by 50% by replacing T700 carbon fiber with glass fiber. The central premise of this project is the desire to produce glass fiber with strength exceeding carbon fiber with half the cost. The approach in Budget Period 1 is to produce this high-strength fiberglass using a new manufacturing process, build and test tanks, and model performance and cost improvements using tank data. In Budget Period 2, the team wishes to improve the fiberglass, build large tanks and test at higher pressure, and investigate safety factors. The approach is reasonable, but it hinges entirely on the team’s ability to produce the required high-strength glass fiber. This ability has not been demonstrated so far. A one-year no-cost extension has been sought to address these shortcomings.
- The approach of evaluating alternative glass fibers that could potentially have better mechanical properties than carbon fibers while being lower-cost is reasonable; however, the project has shown no evidence of proprietary glass fibers that can even achieve properties that are comparable to T700. The project has been in a no-cost extension during Budget Period 1 and still cannot achieve the properties required, so it is not likely that this approach will be successful. The U.S. Department of Energy also recently funded a similar effort through the Small Business Innovation Research program comparing basalt fibers to a T700 COPV, and it added so much weight to the overall system that the automotive companies were not interested in the concept, so it is not clear why this concept is continuing to move forward.

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.

- Substantial difficulties have been encountered with the glass fiber manufacturing process, and a one-year no-cost extension was granted in order for this issue to be addressed. Assuming that these manufacturing issues can be successfully addressed, substantial progress during the next performance period could be expected. The reviewer was not pleased with the comparison to E-glass tanks. While substantial improvement, especially in cycling, was noted with respect to E-glass tanks, it is not clear that this will correlate in any way with performance in comparison with T700 tanks. Testing during the next reporting period must be compared with T700 tanks in order to prove feasibility.
- The approach is valid; however, the strength of the glass is not sufficient to offset the additional weight and additional manufacturing cost required for the added fiber. Sizing technology may help, but most likely not enough to compensate.
- There have been issues with the fiber quality attributed to fiber processing that are not resolved. Despite the fiber quality, prototype tanks were prepared for high-pressure testing. This does not seem to have value.
- Of the various tasks listed, only two tasks have been accomplished to date: (1) novel fiber development and (2) tank modeling and validation. All of the remaining tasks have been delayed. Two types of glass (A and B) with types of binder (I and II) have been created by PPG Industries, Inc. (PPG). Thirty-six vessels have been made at Hexagon Lincoln; however, the size of these tanks was not specified. Also, it is vexing that nowhere is the design operating pressure of the tanks presented. It was found that while glass fiber A and B had a pristine single fiber strength of 5357 MPa and 5583 MPa, respectively (exceeding that of T700 carbon fiber of 4900 MPa), unfortunately, there was a 40% loss of strength in translation. This loss of fiber strength is a huge setback. If it cannot be addressed, then clearly the entire project is in jeopardy, and the stated goals will not be met. The principal investigator (PI) compared the high-strength glass fiber tank performance against reference E-glass. It is not clear why the team wants to compare against E-glass. The team's stated objective is to exceed T700 performance, so all comparisons must be made against T700 tanks and not E-glass.
- The PI acknowledged that PPG has had many problems manufacturing the glass fibers but could not provide a reasonable path toward success. Therefore, this project does not seem to be producing reasonable accomplishments and has no clear pathway to achieve success.

Question 3: Collaboration and coordination with other institutions

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

- The partnership between PPG, Hexagon Lincoln, and Pacific Northwest National Laboratory (PNNL) seems to be working well.
- The team collaborates with a tank manufacturer and a national laboratory, which is very useful.
- The project seems to be clearly utilizing the expertise of PNNL to guide some of the evaluation of designs and utilizing the expertise of Hexagon Lincoln to develop tanks. However, without actual material, there is not a clear pathway for continued collaboration.
- The partnership with Hexagon Lincoln for tank production is functioning well, as is the experimental stress rupture work being done with PNNL. The role of PNNL beyond this experimental work was not described in the slides/oral presentation.
- The team includes a high-level tank fabricator and DOE laboratory technical support.

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

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

- The desire to produce safe, reliable, and cost-effective hydrogen storage tanks is well aligned with DOE objectives.
- The ability to produce high-strength glass fiber that could replace the carbon fiber is expected to reduce tank costs.
- If the project is successful, a dramatic cost reduction for 700 bar hydrogen storage would be possible. However, the impact of the associated weight penalty on driving distance (anti-lightweighting) should also be considered.
- The project seems to align somewhat with the DOE efforts to lower costs, but it is not completely apparent that these high-density glass fibers, combined with the safety factor of 3.0, will ever be viable candidates to supplant T700, so the potential impact is probably lessened by this fact.
- The approach and relevance are appropriate, but the results are not as encouraging as hoped.

Question 5: Proposed future work

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

- Future work appears reasonable. It very much relies on solving the manufacturing issues encountered to date.
- The path forward for PPG to overcome the manufacturing hurdles of producing adequate glass fibers was not clear. It seemed that the company was not completely supportive with moving forward on this project and re-evaluating, so the prospects for future work are unclear.
- Everything hinges on the researchers’ ability to produce high-strength glass fibers with low translation loss. If they cannot solve this technical challenge, then the whole project is in jeopardy.
- Glass-fiber-based tanks may be more appropriate for hydrogen refueling storage or delivery to replace steel. The added tank weight does not seem appropriate for transportation systems. The project needs a business model.
- There exists no concrete plan to tackle the quality issue of the fibers themselves. Continuing tank testing despite the fiber quality issue is not productive.

Project strengths:

- PPG has expertise in glass fiber manufacturing, which can be leveraged to produce hydrogen storage tanks with low composite cost compared to carbon fiber.
- The project has significant potential for system cost reduction.
- Having both the know-how and a production facility for glass fiber are project strengths.
- The project is good from the standpoint of fiber cost reduction.

Project weaknesses:

- Manufacturing difficulties have been substantial. While it seems that there is a path to success, a good deal of uncertainty remains. Lack of comparison to T700-based tanks is still an issue. It is not clear why the team is building and testing tanks with sub-performance fiber.
- The project seems to have limited progress and coordinating issues.
- High translation loss in glass fiber strength has proven to be a major impediment to progress.
- The project relies too much on materials development rather than on tank design and testing.

Recommendations for additions/deletions to project scope:

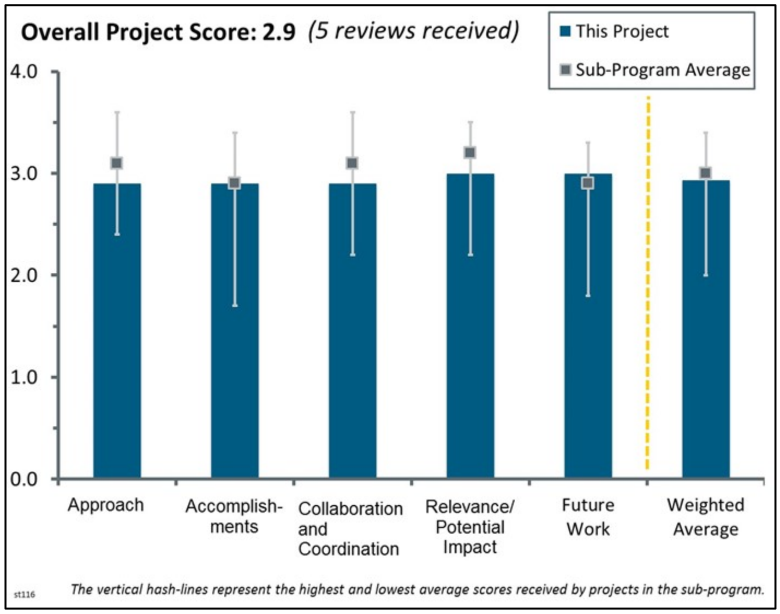
- It is hoped that the team can successfully address glass fiber manufacturing issues to produce fibers with low translation loss.
- The project needs to examine the business case and best application for the glass fiber.
- The project should consider the impact of the weight penalty associated with changing to glass fiber from carbon.
- It is recommended that focus be directed on improving the quality of the fiber for a proof of concept. In addition, the impact of the glass fiber on the tank’s weight should be addressed.

Project #ST-116: Low-Cost α-Alane for Hydrogen Storage

Richard Martin; Ardica

Brief Summary of Project:

Overall objectives of this project are to reduce production cost of α-alane (aluminum hydride, or AlH_3) to meet the U.S. Department of Energy (DOE) 2015 and 2020 hydrogen storage system cost targets for portable low- and medium-power applications. Results will enable broader applications in consumer electronics (e.g., smart phones, tablets, and laptops), back-up power, unmanned aerial vehicles, forklifts, and vehicles.



Question 1: Approach to performing the work

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

- A well-explained, justified, and focused approach lends credibility to the overall effort. For example, the approach for using a moving particle bed electrochemical reactor was justified, as it enables improvements in process kinetics (e.g., throughput, reactor size, etc.), important considerations for commercialization. The approach to estimating costs, including commercial-scale estimates provided by Albemarle, was well characterized and well presented, lending confidence in the outputs.
- The approach to estimating costs seems to follow standard procedures and incorporate the relevant processing steps. The overall approach addresses the objective of lowering alane cost through the electrochemical synthesis method at a relevant scale. This effort is directed at addressing DOE barriers and targets in portable power.
- The presentation this year was improved with greater detail provided in both the Annual Merit Review (AMR) slides and reviewer-only slides.
- Little was known about the electrochemical process for alane production developed at Savannah River National Laboratory (SRNL) at the time Ardica performed their original, limited economic analysis of the industrial-scale production of alane by this method. As more information about the chemical, physical, and mechanical complications of this system has come to light, the promise of this approach to low-cost production of alane has become increasingly dim.
- The project has developed a detailed cost model for alane production via the electrochemical route. The projected cost ($56/kg alane) is about 50% lower than that produced by the chemical route. The key model assumptions and parameters, however, should be independently verified by a third party such as Strategic Analysis, Inc. At the highest production level of 3200 MT/yr, the cost model predicts a cost of $30/kg alane, which is three times higher than the target in project milestone M1.03 preceding the go/no-go decision. If there are no major changes to the manufacturing process for achieving the cost target, a no-go decision should be considered.

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

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

- The project made good progress in three areas: (1) much-improved details (compared to 2015 report) in the cost model, (2) fabrication and operation of the particle bed, and (3) partial recovery of alane-

tetrahydrofuran (THF) adduct from electrochemical cells. A main challenge that needs to be overcome and demonstrated is the regeneration of $LiAlH_4$ from the products deposited on the cathode.
- Working with project partner SRI and a University of California (UC), Berkeley, researcher, Ardica designed, built, and operated a moving bed electrochemical reactor and characterized its performance with respect to key parameters (e.g., particle size, electrolyte, electrolyte flow rate, etc.), thereby providing not only proof of principle but also early experimental guidance on the cost/process analysis of a scaled-up process. The cost analysis described was derived from a credible process flowsheet developed with the project's commercial collaborator, Albemarle, and yielded information valuable to determining research and development needs to reduce costs, improve throughputs, etc.
- The team has analyzed a significant number of variables providing some guidance to direct where research should focus to get the most advantage. Some discussion at the end regarding the need for work on reducing cell resistance without the need to worry about cell potential could have been handled much better. Ohm's law would suggest that resistance (R) and voltage (V) would be directly proportional.
- Progress in mapping a potential (electro) chemical process with all relevant materials and methods appears good, although it is not clear that some of the individual steps have been designed in a final scalable manner. Progress in demonstrating new efficient process steps in appropriate scale is sporadic and largely constitutes a series of one-off results. The project aims to "maximize" $LiAlH_4$ recovery; results point to characterization of cathodic products. The project also aims to "optimize" the fluidized reactor; results indicate a design has been chosen that will facilitate evaluation of various parameters, so perhaps optimization will occur. With the project more than 50% complete (even at slide submission), there is a need to make further progress in a prototype reactor that allows realistic evaluation of alane production rates and yields and that actually produces alane (or at least the adduct) in sufficient quantities (perhaps kilograms) to give confidence in the economic assessment. Recrystallization of the adduct is also needed at scale for the same reasons.
- The economic analysis reported this year was a vast improvement over the analysis that was presented a year ago. However, as came out during the question-and-answer period, several experts feel that the costs of the recrystallization, hydride recovery, alane separation, electrolyte recovery, and/or alanate regeneration are still significantly underestimated. Even more concerning is that the effort to develop an electrochemical cell with high enough performance to meet system targets is still in the notional design phase. As a result, a heavy component of the "capital costs" portion of the cost estimate is based on a guess of the cost to produce "a scaled-up version of a prototype of a yet to be fully designed particle bed electrochemical cell." This makes the whole cost estimate unreliable.

Question 3: Collaboration and coordination with other institutions

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

- The end user, Ardica, clearly has an excellent collaboration with SRI International (SRI), who has a very good collaboration with Professor Evans at UC Berkeley and with Albemarle, who is looking at the cost and process modeling. The collaboration with SRNL was less well defined, and it is not clear whether there is any discussion between SRI and SRNL, or whether any is needed.
- There is good collaboration with SRNL and other partners.
- There seems to generally be good communication between SRI, Ardica, and SNRL. However, it was disconcerting that the SRI presenter said that the problem of dendrite formation persisted right after the SRNL presenter told us this problem had been solved. Professor Evans is a very nice addition to this team.
- There was some discussion about conference calls between Ardica and SRNL but not much discussion that included SRI.
- Communication with partners appears good, but the evidence for effective collaboration is not so great. The use of THF is an example of good coordination, but SRNL appears to be working on a different adduct for recrystallization. There is no mention of the MgNi cathode development presented by SRNL in the current project—this may need to be incorporated. SRNL also claims $LiBH_4$ (as well as $LiAlH_4$) is critical for recrystallization; this was not apparent in the detailed chemical process plan. The partners also seem to be duplicating some work. Perhaps there is an opportunity for some separation of effort here, with one partner focusing on a critical step that the other requires. Collaboration with UC Berkeley appears more straightforward, with this partner providing advice on reactor design.

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

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

- The project goals support DOE goals in portable power though cost-effective regeneration of a high-capacity storage material.
- Although alane has an extremely high energy density, its use as an energy carrier is impractical because of the high cost of its production through standard chemical methods. The novel electrochemical process for the production of alane discovered at SRNL might change this situation. Thus, an attempt to develop a practical, low-cost process version of the SRNL electrochemical process is of high relevance to the DOE goal of developing advanced hydrogen storage systems for fuel-powered portable electronic devices.
- There is good potential for this project to provide a viable material that meets the targets for medium- and low-power applications for the U.S. Department of Defense and others, making this a very relevant project for DOE. As the approach is well defined and the accomplishments are timely and appear to be leading to progress toward viable processes, this project may also end up having an impact in the storage media field.
- This project is relevant to portable low-power systems that use alane as a hydrogen storage material. The cost of alane is prohibitively high for light-duty automotive applications.
- The project appears to align with the needs for small power, and the main target for research seems to be the U.S. Army; it is not clear why this is being funded by DOE.

Question 5: Proposed future work

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

- The future work is well posed, concise, and logical. The team appears focused on critical issues (e.g., kinetics, yield, recyclability of solvents and reagents, etc.) that the team's process spreadsheet indicates result in reducing costs.
- The future work proposed is generally appropriate and directed toward overcoming barriers. It is somewhat generic, and there is little evidence of detailed planning, decision points, or risk mitigation strategies.
- The proposed future work is on target, but it will be difficult to complete it within the time and budget remaining for this project.
- In the remaining time, the focus on the reactor is important.
- The proposed pulsed method reduces process efficiency considerably. The project should look into mechanical methods for removing and collecting dendrites.

Project strengths:

- The project is focused on key parameters that will enhance throughput and reduce process costs. The team and collaborations are good.
- The team has considerable experience in alane synthesis and is very focused on solving the technical issues.
- SRI has vast experience in the development of alane syntheses.
- There is detailed consideration of processes for economic assessment, although some of the steps are still being worked out. There is focus on materials and processes with potential to have an impact on DOE goals.

Project weaknesses:

- While much of the work has been to demonstrate proof of principle for various aspects of the process, there was little shown or discussed about what the path to scale-up might comprise. It is hoped that the next review will include more experimental evidence that scale-up is occurring and achievable.
- The presenter seemed to be missing the point of several questions. In the future, he needs to be more direct with answers. Asking someone if he/she is a reviewer and then telling him/her to look at the reviewer-only

slides comes across as less than genuine and leaves the audience wondering if there is an answer or just a weak knowledge.

- Progress in the scalable reactor appears to be somewhat empirical, with little evidence of a carefully planned approach. Collaboration could be more effective with partners contributing complementary results.
- Regeneration of $LiAlH_4$ could be a major road block in terms of cost and efficiency.
- The limited initial understanding of the SRNL electrochemical process has proven to be a weak foundation for this project.

Recommendations for additions/deletions to project scope:

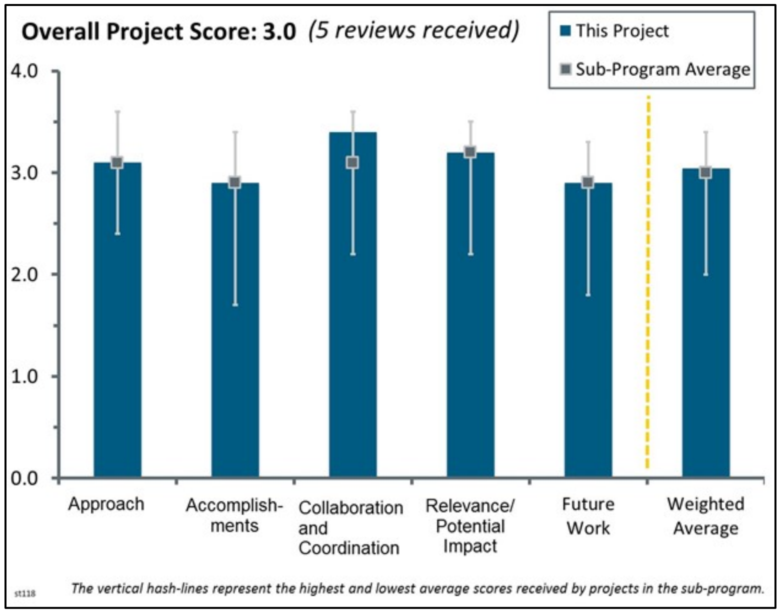
- The project needs clearer division of labor with partners, better division of effort and better incorporation of results from one partner to another, and a more focused effort to build a reactor with high throughput and appropriate product qualities (this is planned but warrants reinforcement).
- The project should incorporate mechanical methods such as scrapers to prevent the dendrite growth problem.
- Some emphasis should be placed on looking into the implications for doing a semi-commercial scale process using high-flammability solvents such as THF; where this figures into the eventual cost is unclear. If THF adduct formation is required and no other solvent substitute can be employed, working with THF could be problematic at scale.

Project #ST-118: Improving the Kinetics and Thermodynamics of $Mg(BH_4)_2$ for Hydrogen Storage

Brandon Wood; Lawrence Livermore National Laboratory

Brief Summary of Project:

The objectives of this project are (1) to combine theory, synthesis, and characterization techniques at multiple length/time scales to understand kinetic limitations and possible improvement strategies in $Mg(BH_4)_2$ with relevance to other light-metal hydrides, and (2) to deliver a flexible, validated, multiscale theoretical model of (de)hydrogenation kinetics in “real” Mg-B-H materials and use predictions to develop a practical material that satisfies 2020 onboard hydrogen storage targets. Current project year objectives are to synthesize MgB_2 nanoparticles with <10 nm diameter, measure x-ray absorption and emission spectra for bulk MgB_2/$Mg(BH_4)_2$ during stages of (de)hydrogenation, and compare measured and simulated spectra on informed models to determine local chemical pathways.



Question 1: Approach to performing the work

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

- The combination of theory, synthesis, and characterization across multiple time and length scales provides a tremendous opportunity to gain a deeper understanding of kinetic processes in $Mg(BH_4)_2$. The research and development (R&D) team understands the barriers and challenges that must be overcome in this system, and the project has developed an innovative research approach and work plan that is fully consistent with achieving success. However, it is somewhat disappointing that work on cycling and reversibility is deemed by the project team to be beyond the scope of this project. Kinetic limitations are being addressed using nanoengineering and catalytic additives. Although this approach is sound, care must be taken to ensure that agglomeration of “free” nanoparticles does not limit kinetics (this was pointed out in the presentation—it is simply being reinforced here).
- The main objective of this work is very ambitious. The multiscale problem, both theory and experiment, presents very difficult tasks, and so far nothing has been completely successful in this area of science. The project’s efforts are appreciated. Trying to separate the different components of the process, particularly from the modeling side, is very hard. The main problem in statistical sampling in theoretical models is the presence of rare events such as diffusion, dissociation, etc. The models are always going to be “toy models” of reality. On the other hand, the experimental part is more solid because it is just observation of reality.
- This work ties in well with the ongoing efforts within both the Hydrogen Materials–Advanced Research Consortium (HyMARC) and the validation team. It is not clear how this work was delineated from the HyMARC effort when the principal investigator (PI) was constantly referring back to HyMARC.
- This effort employs computational approaches to evaluate the energetics and spectral properties accompanying hydrogenation (apparently of at least the initial hydrogen bound to either the surface or edge on slide 11).
- To date, this project has taken a highly fundamental approach, nicely integrating theory, characterization, and synthesis. It has been successful in that it has provided important new insights into the processes controlling the kinetics of the hydrogenation of MgB_2. However, the goal of this project is to make a

significant improvement in the performance of the $MgB_2/Mg(BH_4)_2$ system as a hydrogen storage material. Increasing the kinetics of hydrogenation of only 10% of the material without changing the dehydrogenation kinetics falls very short of this goal. A much more practical approach needs to be adopted in the next year of the project.

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

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

- Initial results and progress are encouraging. Calculations of B-H and B-B bond scission and formation in $Mg(BH_4)_2/MgB_2$ provides important baseline information. Likewise, identification and interpretation of intermediate species is critical to quantifying limitations to kinetics. The demonstration that hydrogenation of MgB_2 under high-pressure conditions can lead to direct conversion to $Mg(BH_4)_2$ is a signature accomplishment that provides an "existence proof" that unwanted reaction intermediates can be suppressed. Initial theoretical studies of phase nucleation and nucleation barriers and interpretation of reaction intermediates through comparison with experiments are providing useful guidance for the experimental work. This is the first project that provides a theory/modeling capability to address reaction kinetics issues in a complex hydride in a comprehensive way. The effort to prepare size-selective nanoparticles seems to be progressing at a slower pace. The procedure for nanoparticle synthesis (surfactant-assisted ball milling and Stavila stripping method) may be too aggressive (brute force) to permit the formation of nanoparticles with a well-controlled size distribution. It will be important to rapidly evaluate the efficacy of this approach for achieving project goals for nanoparticle formation.
- The project should further explore the heterogeneous surface reactions that can occur and how that would constantly be varying the dissociation versus diffusion shown on slide 10 (9). The information on slide 12 (11) began to address this issue. The PI pointed out several times that the issue tends to be that the changes initiated are going to change as hydrogenation occurs. However, this may create a "diffusion" barrier as the hydrogen tries to get into the bulk—but this also means that the bulk is being constantly redefined as hydrogenation occurs—i.e., you no longer have the homogeneous material with which you started. The point at which bulk versus edges/basal planes are defined as hydrogenation is unclear. It is unclear whether new "introduced" materials stresses can be manipulated to generate more basal plane sites. The only reason a 4.0 was not given was slides 16 and 17, on which the equation shows a BH_5^{2-} species. What the PI was trying to picture was clear, and he explained it well in the question-and-answer (Q&A) period. However, it is recommended this be done differently in the future.
- Evidence has been found that indicates that the hydrogenation of MgB_2 occurs on the surface through direct hydrogenation to BH_4^- rather than through a borane intermediate process as occurs in the dehydrogenation of BH_4^-. This is a very significant finding that could be of major importance to the development of this material. On the other hand, the results of the computational studies seem to be predicting processes that do not make chemical sense. Although it was explained that the nonsensical species BH_5^{2-} appeared in the presentation as a typo, it is still not clear that sensible species are being predicted by the computational studies. This underscores that results of the computational studies need to be subjected to critical evaluation and reconciled with fundamental chemistry.
- Segments of MgB_2 are depicted on slide 11. The size of the MgB_2 used to determine the energies is unclear. It is unclear whether there is a binding energy dependence on cell size. It is unclear whether the binding energy is determined for the initial hydrogen atom only. There is no indication as to what would happen if more hydrogen atoms are successively added to the cell. There appears to be a difference in the experimental x-ray absorption spectroscopy data shown on slide 10, which shows a sharp, well-separated pi* transition that is less obvious in the computational spectrum. No explanation of this difference was provided. Slide 13 mentions hydrogenation at interfaces. Given the schematic depiction, this appears to indicate that interfaces means edges in this case. If this is the case, then the interpretation could be that an effective strategy for direct hydrogenation is to maximize a particle's geometry where edges dominate. This would presumably run counter to the notion that a particle morphology that maximizes the normal to the c direction minimizes surface free energy. On slide 16, the issue was raised regarding the molecular fragment stoichiometries and charge depicted in the reaction. It is uncertain these fragments are known to exist in nature.

- Accomplishments include the molecular dynamics (MD) shown in slide 17. If a reaction happens spontaneously in a computer simulation using MD, then either the model is very wrong or the material reacts spontaneously. This is dealing with rare events. The model should be revisited. Phase nucleation is probably going to be a big problem: how to determine the energetics and kinetics of the interfaces between phases, hydrogen transport, etc. The sampling of possible structure combinations is enormous and unlikely to be possible in a rigorous way (slides 20 and 21).

Question 3: Collaboration and coordination with other institutions

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

- The collaboration within the project team is excellent. There is good communication with other groups doing related DOE work.
- Extensive collaborations exist with other HyMARC partners and external institutions. As new projects are folded into HyMARC, this project will undoubtedly serve as a centerpiece for enhanced collaboration and cooperation among all participants. Understanding sorption thermodynamics and kinetic processes in the $Mg(BH_4)_2$ system is particularly challenging, and it requires the full complement of capabilities available in the HyMARC project.
- The experimental partners are solid. The connection between the Nuclear Magnetic Resonance confirmation and some vibrational spectroscopy is not properly explained. It is just stated and used for fingerprinting. In order to reproduce the experimental data, addition of a modeling demonstration is necessary.

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

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

- This effort is an integral part of a vital project, HyMARC, and for the overall DOE Hydrogen Storage program. The project is providing the consortium with a powerful means to obtain a deeper understanding of the fundamental processes operative during sorption reactions in complex metal hydrides. Likewise, this project offers a pathway to guide future work on emerging systems. It has significant potential to advance progress toward achieving DOE goals. The work on $Mg(BH_4)_2$ is especially important because this system is among only a few complex hydrides that has potential to meet DOE storage targets.
- The $MgB_2/Mg(BH_4)_2$ system currently is the most promising candidate among the complex hydrides with potential to meet DOE targets.
- The choice of material seems to be driven by the old-fashioned “weight percent” criteria, i.e., it has a good deal of hydrogen, so an important step is to see how to get the hydrogen out, nanosizing, etc. This is unlikely to be a useful material itself. It seems to be more of an academic interest (which is necessary and very important but at odds with “impact in real life”).

Question 5: Proposed future work

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

- The proposed effort to develop and improve catalysis in the next phase of the project is a good step toward its becoming more practically oriented. However, further studies should be focused on overall hydrogen cycling performance and not just the hydrogenation or dehydrogenation half-cycle.
- The proposed future work is provided mainly in sentences given at the bottom of a few of the “accomplishment” slides. That makes it difficult to offer a thoughtful and complete review of the proposed work. That being said, it is fairly straightforward to “read between the lines” and understand at least to a reasonable level what is planned for future work on the project: alternative microstructures with interfacial transport paths, deeper understanding of phase nucleation processes and barriers by incorporating stress and interfacial penalties; exploration of why there are differences in results from experiment and theory for

stability of intermediates; etc. A more concise and self-contained summary of future work would be helpful.

- Most of the problems have been identified. It is still uncertain whether it can be done. Furthermore, if we understand the formation of the hydrides, it is unknown if it can be made to work.

Project strengths:

- A very strong team with extensive expertise and capabilities in theory/modeling, materials synthesis, and characterization/testing is conducting research on this project. The investigators are well-versed in the challenges and issues that must be overcome for a complex system such as $Mg(BH_4)_2$ to ultimately be successful as a practical hydrogen storage material. The integrated experiment–theory approach is powerful, facilitating progress toward gaining a deeper understanding of the critical kinetic processes and rate-limiting steps operative during hydrogen sorption reactions in $Mg(BH_4)_2$.
- It is a combination of state-of-the-art techniques from the modeling point of view. It aims to study materials and processes in great detail. Results could be transferable to other systems.
- The PI and the team are excellent. The additional efforts at HyMARC can only serve to move this forward.
- This project has an excellent core of integrated fundamental theory, characterization, and synthesis efforts.

Project weaknesses:

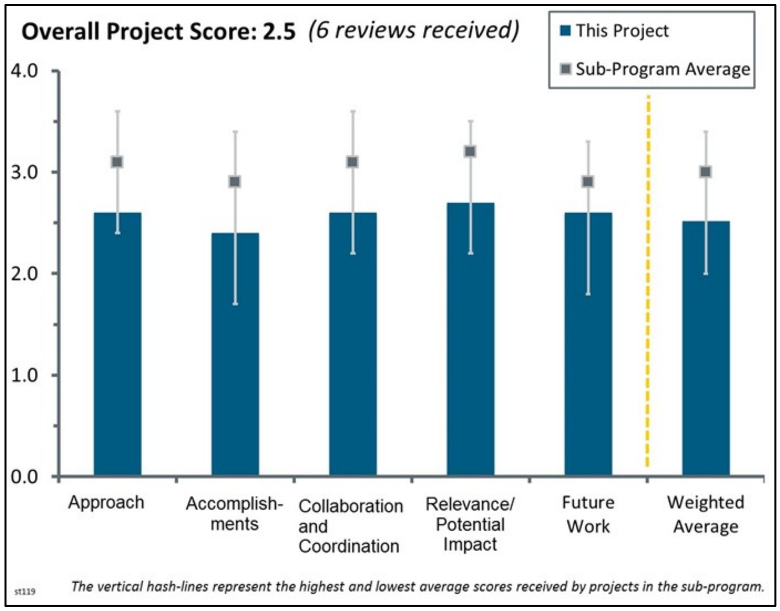
- Although the project team is especially strong in theory/modeling, metal hydride synthesis, and surface characterization, there seems to be limited expertise in the chemistry of metal hydride systems. Bringing in an individual (or individuals) with a deeper understanding of complex metal hydride chemistry would be beneficial. It was stated during the presentation (Q&A) that studies of reversibility and cycling are beyond the scope of the current project. However, these issues should not be ignored or marginalized (cycling efficiency and reversibility are DOE mandates). For DOE's hydrogen storage application, these issues are every bit as important as understanding thermodynamics and kinetics issues. In fact, cycling/reversibility studies provide an indirect way to explore the presence and evolution of rate-limiting intermediates. It is important for the project team to consider expanding the scope to include at least limited studies of cycling and reversibility.
- The project is oriented toward incremental advances in the fundamental understanding of the system, rather than producing a significantly improved hydrogen storage material.
- The observation of hydrogen using x-rays is indirect. This is probably not the best choice, in particular when it comes to comparing theoretical models. Statistical sampling of rare events and energetics of a large number of possible structures is very difficult; a calculation of few structures needs to explain $>10^{23}$ atoms in real life and be predictive. It is a hard problem, and the approach is over-selling the capabilities of theory.
- Stronger interaction with Jensen/Autrey in the future is suggested.

Recommendations for additions/deletions to project scope:

- The project can use additional complex hydride chemistry expertise (either via collaboration, a new funding opportunity announcement project, or addition of a staff member). The project can expand the scope to include at least preliminary studies of cycling and reversibility.
- The project should address the statistical sampling of structures in the models at the ab initio methods level. That way, the project can try to validate the models in a more convincing way.

Project #ST-119: High-Capacity Hydrogen Storage Systems via Mechanochemistry

Vitalij Pecharsky; Ames Laboratory



Brief Summary of Project:

This project is developing novel high-hydrogen-capacity silicon-based borohydrides and composites with the aim of achieving low-cost, high-performance hydrogen storage materials. Silicon-based borohydride materials are predicted to have borderline thermodynamic stability. Researchers will use stabilization strategies based on hypersalt formation using alkali and alkaline-earth cation additions to bring the enthalpy of desorption into the targeted range. The project will also investigate borohydride/graphene nanocomposites that utilize graphene's advantageous properties.

Question 1: Approach to performing the work

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

- The project aims at making high-capacity Si borohydrides via mechanical chemistry (ball milling) and substitution of alkali and alkaline earth elements to help stabilize them. There are calculation, synthesis, and programmed hydrogen desorption components of candidate materials. This is a new idea, never tried before, and certainly has the theoretical potential to meet DOE targets at reasonable desorption temperatures. It is a high-risk, high-reward effort and is certainly worth trying. The chemistry is complex and sometimes not predictable and calculable. The project seems hard to judge as to feasibility and not very integrated with other DOE efforts.
- The investigators have approached the project exactly as proposed: first using computational methods to determine potential candidate materials, followed by related mechanochemistry experiments.
- This project is based on the shaky foundation that the targeted borohydride compounds will undergo *reversible* dehydrogenation and that they can be synthesized by ball milling techniques. Unfortunately, this is not consistent with the findings of the worldwide effort over the last 10 years to develop mixed metal borohydrides. Hundreds of mixed-metal borohydrides have now been synthesized, and none of them has been found to undergo reversible dehydrogenation. Recently, this was found to be due to the concurrent elimination of diborane upon thermal dehydrogenation. Furthermore, successful syntheses of lightly stabilized aluminum borohydrides has been achieved only through low-temperature "wet" chemistry approaches, *not* ball milling. Thus, mixed-metal borohydrides that undergo reversible dehydrogenation and the preparation of compounds with *borderline stabilities* through ball milling seems unlikely. Likewise, the isolation of compounds with silicon in the +2 oxidation state seems unlikely. Finally, this project does not employ the techniques that have become standard in the structural characterization of borohydrides: IR, multinuclear nuclear magnetic resonance (NMR), and structure determinations derived from Rietveld analysis of powder x-ray diffraction (PXD) data. Instead, the approach is to obtain only the raw powder diffraction pattern (that reveals only that LiCl is formed) and inconclusive NMR data and then speculate on the nature of the compounds that are obtained.
- The idea of using computer modeling to identify the stability of phases is not new. This proposal tries to lead the discovery by calculating possible solid compounds and then trying to synthesize them. There is a

prediction of materials that are not known to exist, and the proposed work is to use ball milling to create them. The driving force is the “weight percent” metric.

- The U.S. Department of Energy (DOE), DOE reviewers, and the project investigators should review the literature and work funded by DOE’s Office of Basic Energy Sciences (BES) and accomplished by Savannah River National Laboratory (SRNL) and Virginia Commonwealth University. They have made both Si and Al hypersalts and exploited the benefits of borohydride/graphene composites when using C_{60} for the carbon sources. This work seems merely to attempt to reproduce those efforts.
- The project is aimed at addressing gravimetric capacity barriers and has proposed high-risk materials that could offer progress. The presentation suggests the project aims to improve understanding of hydrogen chemisorption, but there is no evidence of this. The objectives include composites with graphene for thermal conductivity, but without sufficient knowledge of the proposed borohydride salts, the reason for this is unclear.

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.

- During the first project year, many interesting results have been generated using fundamental calculations and mechanochemistry synthesis trials. New stabilized Si borohydride compounds have been made, some of which have promising H-desorption properties. The science being developed so far in this project is very interesting and of potential future use in DOE projects.
- This is an unknown area of exploration and, therefore, there is no guarantee that promising Si-borohydride hypersalts or borohydride/graphene composites will be found. Having said this, it is worthwhile to take this approach to search for such new materials. Despite investigating various systems, there does seem to be only fleeting success as of yet, which is not necessarily the investigators’ fault.
- The researchers have investigated a relatively large number of systems and carried out a good number of computational and physical experiments. However, the computation has made some counterintuitive predictions that are not explained, and the experimental products are not well-characterized, especially in a quantitative sense. The concept of Si^{2+} is not one that is soundly based in chemistry (Si forms covalent rather than ionic products), and it would be good to see some literature precedent for Si^{2+} compounds. Of course, it is sometimes necessary to explore new territory, and the project may be an example of this. The characterization of products does not give much information, especially quantitative. The formation of LiCl does indeed indicate that a reaction has taken place, but to what is not clear. The NMR shows BH_4 remains in some samples and has undergone decomposition during preparation of others. The use of “onset temperature” for hydrogen release is not especially illuminating and could be misleading if this represents a small fraction of the sample. Pure phases of standard hydrogen storage materials (including borohydrides) often show a lower “onset temperature” after high-energy ball milling, but this is attributable to a highly defective surface or amorphous regions that do not survive cycling. The weight changes presented do not represent a progression toward DOE goals. As one of the reviewers noted, the conclusion of no B_2H_6 formation is not justifiable given the experimental protocol and the findings of other groups regarding B_2H_6 detection by mass spectrometry.
- The computer screening shows some metastability of certain compounds. Experimentally, the trials show that most of the systems show far less “weight percent” than the calculations, and some diffraction data seem to support the formation of certain compounds. There is not unequivocal determination of the formation of the SiH_4 species. So far, nothing apart from some calculation-based predictions has been demonstrated. There is no unique set of theoretical models that support the stability of these compounds, so the relative stability can have different orders or not exist at all using other functionals, etc. The evidence that this is true is very thin.
- These efforts have generated only poorly characterized mixtures of materials, the most promising of which *irreversibly* eliminates 3.2 wt.% upon thermal decomposition. In view of the approach that is being taken by this project, the lack of progress is not surprising.
- The accomplishments seem mainly from the theoretical side, and results are not promising for producing the theoretical materials. The team should refer to literature and reproduce SRNL’s results from hypersalts as a starting point, where the real concern is stabilizing these materials.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration with the University of Missouri–St. Louis (UMSL)—a project partner—appears strong. No evidence exists of collaboration with other groups.
- They seem to be collaborating fine.
- It is not clear how to judge this since the project does not stress collaborations with other institutions. Nonetheless, it seems like the project could benefit from other experimental techniques from other DOE-funded entities such as the Hydrogen Materials—Advanced Research Consortium (HyMARC).
- The collaboration with UMSL is adequate and producing most of the results presented so far. However, the recommendation is to pull in institutions that have modeled and produced these materials to ensure this is not just reproducing their efforts.
- Interaction within the project team is good, but otherwise, this effort is quite insular. The inclusion of this project within HyMARC should be a vast improvement in this regard.
- There is only one collaboration partner (Majzoub at UMSL for a priori calculations). The project could use more chemistry collaborations and added outside ideas.

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

This project was rated **2.7** for its relevance/potential impact.

- This is clearly a worthwhile endeavor since the idea has not been explored to any significant extent yet. It is somewhat high-risk but also potentially high-reward.
- The project is certainly relevant to the Hydrogen and Fuel Cells Program and DOE research, development, and demonstration objectives. However, it is a very new approach and too early to predict the potential impact. It is an interesting and worthwhile addition to the DOE storage projects.
- There is currently a scarcity of promising new candidate complex hydrides. Therefore, the relevance of this project is simply the clear need to explore previously uncharted synthetic territory. However, the investigators appear to be unaware of the lessons learned by the study of similar materials. Thus, it is likely they will, at best, learn lessons already learned and, at worst, make preventable mistakes that will cause confusion and be a harmful distraction.
- The materials could have the potential for impact, but it is not certain this project will achieve that level. It is not really clear how DOE could fund this project with the understanding that BES has already funded these efforts, and it does not seem that this project is advancing the state of knowledge beyond that which is known.
- This is a very unlikely set of compounds from a chemist’s point of view. It is not proven that they can even exist from a simple energetics point of view, not to mention that it is even more unlikely that they will have the right kinetics. If any of these compounds can be formed, it could be of some interest from the point of view of an example of the methodology. However, proving that the methodology is correct requires far more than few examples.
- The project is a high-risk effort to discover new materials that can meet DOE targets. However, results to date do not give confidence that this will pay off.

Question 5: Proposed future work

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

- Proposed future work seems reasonable with respect to the funding provided.
- The proposed future work plans are very reasonable. However, the planned borohydride/graphene composite work may detract from the main Si borohydride mechanochemistry challenge.

- The plans to confirm the identity of products and to apply some quantitative analysis are what this project needs. Reversibility is of course a good aim; however, this could come later once it is clear what has actually been synthesized.
- In view of what has generally been previously found for mixed-metal borohydrides, the proposed efforts to isolate the products from the ball-milled reaction mixtures and to grow single crystals are unlikely to be successful.
- This is more of the same that has been done in the first part of the project.

Project strengths:

- Project strengths are the following: a potentially new class of promising compounds is being explored; the combined theory/mechanochemical approach seems highly appropriate to the task; and the investigators are known to be competent researchers in the field.
- The aim is a completely new class of materials with potentially very high gravimetric H-contents.
- The project is making an attempt to make novel compounds to try to meet DOE goals.
- The project uses computer modeling to drive the discovery of materials.

Project weaknesses:

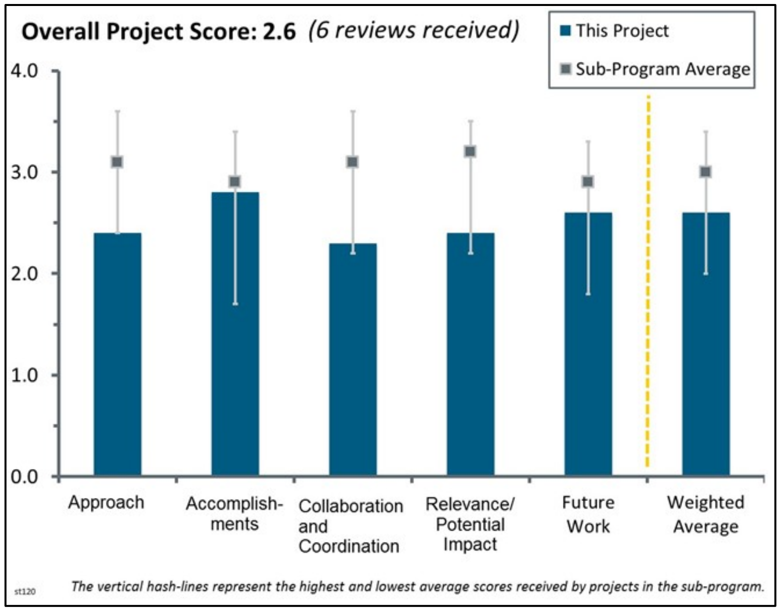
- The project is high-risk. It will likely take much longer than the project timeframe to see whether these materials have practical potential to meet DOE goals for vehicles.
- Characterization of products is poor (particularly quantitatively) and not aided by presentation of results (all the blue-stripe x-ray diffraction patterns are extremely difficult for a reviewer to interpret, for example). The concentration on initial decomposition temperature instead of temperature to release a stoichiometric quantity of hydrogen is also a weakness.
- Project weaknesses stem from the limited success so far. It seems clear that more characterization techniques and more experiments are still needed to find out what is being formed. The investigators would benefit from using outside help from other potential DOE partners, such as HyMARC.
- It is a very simple approach: trying to characterize the energetics and extrapolate to the stability of phases. There is no exhaustive search of other models, etc. It is not a unique, accepted, and well-defined theoretical tool.
- The project team does not appear to have a grasp on the vast, recent body of papers that has appeared on mixed-metal borohydrides in the last eight years.

Recommendations for additions/deletions to project scope:

- The project needs to take a more quantitative approach, starting with a mass balance of reactants versus products. Product mixtures need to be much better characterized, as is planned (and perhaps more so). The recommendation is to concentrate on this aspect first and not investigate composites with graphene.
- Perhaps there should be a little more outside collaboration. The borohydride/graphene composite work could be deleted to allow more time on the main Si borohydride mechanochemistry effort.
- The project should drop the borohydride/graphene composite tasks if they get in the way of any Si-borohydride advances. The investigators mentioned that there are no precursors with Si^{2+} available. If they have not already, the team could look into $MSiH_3$ salt compounds.
- The project should be terminated.

Project #ST-120: Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

Brent Fultz; California Institute of Technology



Brief Summary of Project:

This project aims to address challenges related to the volume of onboard hydrogen storage systems and the low temperature and low enthalpy of adsorption. Researchers are designing and synthesizing materials with high capacities for hydrogen physisorption. The focus is on graphene rather than activated carbon as single-layer graphene is a platform with an excellent surface-to-volume ratio. The project will use graphite oxide chemical routes and plasma approaches to synthesize and functionalize the materials.

Question 1: Approach to performing the work

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

- This is a new project with an approach to "functionalize" single-sheet graphene. The focus appears to involve deposition of single metal atoms on a graphene surface. The principal investigator (PI) shared progress in setting up a laboratory to measure sorption of hydrogen onto metal-doped graphene, as well as a project plan providing some insight into what has been accomplished and what is planned over the next months. This was a good start, but more details would be extremely helpful.
- The systematic approach proposed by the authors is refreshing.
- The guiding hypothesis for this project is not at all clear from the presentation. It is agreed that graphene has a higher surface-to-volume ratio, which should favor uptake of hydrogen, but no support is provided for the somewhat broad statement ("functionalize it") on slide 5. It is not clear *why* it should be functionalized and with what rational design principle. Treatment using graphite oxide chemical routes and the plasma physical approaches will no doubt change the material, but no clear reasoning is presented to indicate why this should improve hydrogen adsorption. The deposition of gold nanoparticles on the surface is also puzzling. It is well known that gold atoms and clusters diffuse across graphite and graphene surfaces with very low activation energies (e.g., see Jensen et al., *Surface Science* 564 [2004]: 173–178). Consequently, it is likely that clusters will form at low-energy locations, such as edges (Zhang et al., *Phys. Rev.* B 81, 125425 [2010]) or steps (P. Jensen et al., *Phys. Rev.* B 70, 165402 [2004]). Perhaps that is the intent, but it was not made clear. Recent experiments suggest that three-dimensional (3D) island growth will result because of the very low adsorption energy on graphene and high coalescence energy of gold (Liu, *Phys. Rev.* B 86, 081414(R) [2012]).
- The project seeks to use single-layer graphene to support metals for enhanced hydrogen storage. The project uses several techniques to methodically step through each treatment process and catalogue everything that can be catalogued. It is not clear what utility this will bring in the long term, and some hydrogen uptake results and/or characteristics would be more meaningful and are urgently needed for the project.
- It is unclear whether the functionalization will be successful. It is unclear whether the functionalization is aiming for addition of atomic metal sites or nanoparticles. Furthermore, there exists the possibility that agglomeration of the metal additives will occur, resulting in low-surface-area features and formation of metal hydrides. It is not clear how this will be prevented. It is unclear whether the metals to be used for

functionalization—which, based on slide 8, appear to be heavy (Au, Cu, Co, Ni, Zn)—will achieve high gravimetric densities. It is not certain that this approach can achieve high volumetric densities.

- There are two major problems: the lack of defect sites in graphene, and the assumption that the gold is generating atomic Au at the surface. These are the cornerstone assumptions of the project. It was not proven in accomplishments that these assumptions are valid. Overall, the project was not well defined.

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 appears to be on track, based on the milestones. Synthetic approaches projected to be tested at this stage of the project have been completed. New Sieverts apparatus was installed, and a method of rapid screening of materials based on single-point measurement was demonstrated.
- Progress has been good. However, the project should look into some questions about the distribution of gold atoms on the surface. Density functional theory calculations and experiments from Manchester suggest that it is difficult to avoid clustering of gold atoms unless the graphene is a few layers thick (Zan et al., *Nanoletters* [2011] dx.doi.org/10.1021/nl103980h).
- This was perhaps the most organized part of the presentation. It would have been better if there were more insight into specifics of how the laboratory setup was going to be used to demonstrate future progress toward DOE goals.
- Given the way this project is progressing, it is difficult to assess whether it is strongly moving toward DOE goals. The project has been active for only about eight months. Clearly, hydrogen adsorption characterization has not been strongly emphasized as yet and needs to be more aggressively pursued. The rather simple single-point isotherm analysis is not a new concept and has been discussed in the hydrogen storage centers before. That it was a milestone was surprising. The PI detailed some interesting results for the graphene preparation (i.e., of high quality) and some hard-to-understand results of Au on these sheets. There is very little evidence that Au atoms exist individually, as they usually coalesce into particles (one known exception being a particular surface reconstruction of an iron oxide surface) unless very cold. It is not clear that this approach will work as intended, and more than transmission electron microscopy images are needed to characterize this.
- Reaction schemes are needed, not pictures of the reactions in the laboratory. On slide 11, it seems the plasma may generate a series of defects in the material. Also, with a 300 keV beam, the particles will move around—and the beam can introduce more damage to the substrate. On slide 12, in the bright field there are typical particles agglomerated on the surface, ranging in size from 1–5+ nm. It is surprising that the dark field image on the right of what is apparently the same region does not show these bigger particles. The interpretation that the small lighter areas are atomic gold is a stretch—it appears to be more just how the graphene is wrapped around the grid, as well as the depth of field. It is highly unlikely that the gold would not agglomerate because of surface energy effects. On slide 14, a large distribution of 1–2 nm particles is visible on the surface, indicating not-unexpected movement. The beam is heating the metal and graphene indirectly, causing an Ostwald-ripening-like effect. On slide 15, the same activation process has been performed as one would use for activated carbon.
- Work on functionalization has not progressed very far. Some careful benchmarking studies have been completed.

Question 3: Collaboration and coordination with other institutions

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

- The project does not currently rely on significant external coordination. Ted Baumann and Robert Bowman were listed as collaborators, but there was little insight into the roles. The PI also works with Channing Ahn, who has expertise in both sorbents and metal hydrides and would be valuable to consult to prioritize specific metals to focus efforts.
- This seems to be a mostly self-contained project, so extensive extramural collaboration is not expected/not applicable.

- The PI may want to consider relying more on the expertise of Ted Baumann or Channing Ahn to characterize the materials.
- The project involves a collaboration with Lawrence Livermore National Laboratory (LLNL), but no evidence was provided that this provided any benefit to the project.
- There seems to be little interaction with anyone outside the PI's own laboratory. No collaborative results were presented.

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

This project was rated **2.4** for its relevance/potential impact.

- Graphene is a relatively new material, and its potential for hydrogen storage is not fully characterized. Consequently, this project seems to align well with Fuel Cell Technologies Office goals, given the relatively low level of information available for this material. Given the uncertainties associated with the approach indicated above, however, the potential impact is still rather unclear.
- There is a very basic effort here that has not really been at the pace needed for DOE to realize its goals. The basic nature of the work is needed—it would be excellent to see whether this approach has promise—but the actual hydrogen results are absent so far.
- This is a basic science project with an interesting methodology. However, it is not obvious that a clear pathway to a new material is emerging at this stage.
- There was some discussion as to why graphene chosen as the support. The weakest part of the presentation was why specific metals are under consideration.
- Until the PI has proven his claims, this work will not be taken seriously. Too much past history on spillover graphene oxide, and the relevant fuel cell work on platinum-group metal/substrate interactions were not considered.
- The presumption is that functionalization of graphene/graphene oxide could increase hydrogen storage density. However, the potential gains over conventional carbons were not clearly identified in the presentation.

Question 5: Proposed future work

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

- Only milestones were given, and these are reasonable.
- Emphasis should be placed on materials that could yield high gravimetric capacities: functionalization using lightweight elements or those that can bind multiple hydrogen molecules. Estimates of volumetric performance should be provided, too.
- Proposed future work is not described in any detail. The only information provided is the project plan on slide 8. This, however, is not cast in the form of a timeline, so it is unclear what work will be the focus during the coming year. Most of the project elements seem to make sense, but the atomic layer deposition TiO_2 work seems out of place; no mention of it is provided anywhere else in the presentation.
- The PI should carefully consider a more specific hypothesis and more specific research goals. These may be known but were not well explained in the presentation. The concept that is being tested was unclear. It could have been room temperature sorption, multiple metal sites, particle size, optimized dispersion of metal particles, etc.

Project strengths:

- The project focuses on a novel material (graphene) with potential for high surface area and functionalizable groups. Results obtained during the previous year indicate that the experimental strategies are working; surface areas increased considerably after activation, and gold nanoparticles were successfully deposited on material surfaces.

- The project aims to develop new hydrogen adsorbents. If successful, this could lead to lower-cost hydrogen storage systems. Using graphene/graphene oxide as the skeleton material could enhance thermal transport during refueling.
- The project has a systematic approach, enhancing gas–surface interactions.
- Strengths are simple assumptions that can be easily tested; good characterization.

Project weaknesses:

- Weaknesses include the PI's apparent inexperience with the importance of the Annual Merit Review (AMR) and the opportunity to show reviewers sufficient information in a 15-minute presentation. The PI needs to ask for, and listen to, advice of collaborators with years of experience. It was obvious from the AMR presentation that there has been very little interaction with collaborators. The discussion with reviewers at end of the presentation lacked detail. The PI did not clarify the rationale for the planned future work when given the opportunity. The PI showed a beautiful high-resolution image of the carbon matrix, but the resolution shown for the Au atoms appeared to be lower, leaving the audience and reviewers in some doubt as to the PI's claims of distribution. There was no scale bar on the graphene image, and the reviewer cannot recall whether the image was from the PI's laboratory or an image taken elsewhere to illustrate the nature of the graphene surface. It was also disappointing that the PI was not better able to answer questions about keeping metal clusters dispersed on the graphene matrix. If this data were presented to a journal for peer review, there would need to be more connection to previous published work. The PI did not appear to know much about the published work in this area, or if he did, he did a poor job of putting his work into perspective.
- The project's rationale and guiding hypotheses are not well defined. The approach seems to ignore existing literature. Collaborations appear to exist only on paper. The project lacks a theory element that could guide synthesis.
- The AMR presentation was missing some aspects that might be better considered next time around and have a more hydrogen-centric presentation with more results. The approach was relatively simple, but a series of X's in a table with no real indication of meaning or results is not helpful.
- Stability of the functionalization (via agglomeration into bulk metal) is a concern. A second concern is that the projected performance gains are unclear.
- There were too many claims without experimental evidence.
- The path to a final material is a bit cloudy.

Recommendations for additions/deletions to project scope:

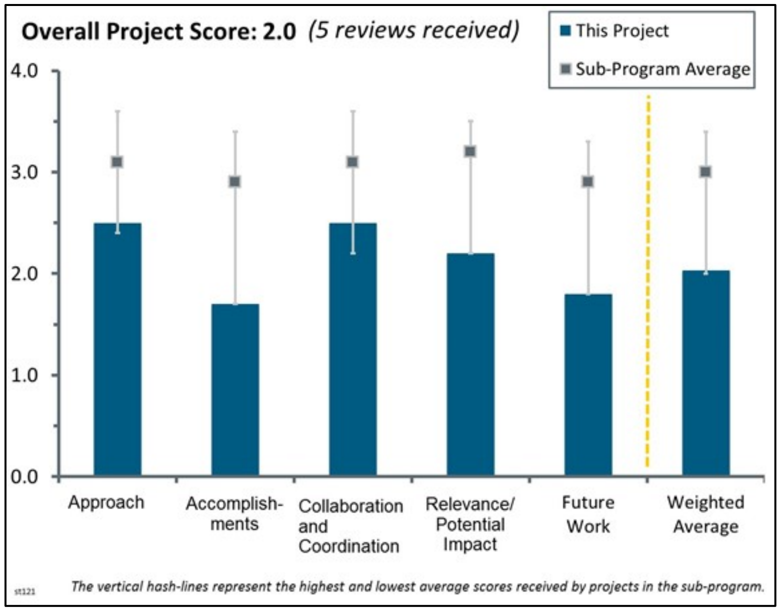
- Clear hypotheses needs to be defined (or at least articulated). The investigators should consider the implications of existing literature concerning the mobility of gold and other metals on graphite and graphene surfaces and use this information to guide experiments. A theory component would be beneficial. Advantage should be taken of the collaboration with LLNL, presumably to provide high-surface-area carbons. The contribution of Bob Bowman needs to be defined.
- There are likely some very good ideas behind the work plan. However, the PI must understand that the AMR is a review. It is important to lay out work illustrating accomplishments, approach, collaborations, and future work. The reviewers are there to help make the project better, but it is hard to help if one has to guess what is happening. DOE could ask the PI to review projects in the next AMR. This would provide a good opportunity to appreciate how to present all the information needed for a thoughtful AMR presentation.
- The project should clarify the steps to achieving a 3D functional material.

Project #ST-121: High-Capacity and Low-Cost Hydrogen-Storage Sorbents for Automotive Applications

Hong-Cai (Joe) Zhou; Texas A&M University

Brief Summary of Project:

The project is designing robust hydrogen storage materials—high-valent metal–organic frameworks (MOFs)—that offer the potential to meet the U.S. Department of Energy's (DOE's) gravimetric and volumetric targets. Researchers aim to determine strategies that allow materials to exceed the traditional limits of carbon-based materials (1 wt.% hydrogen per 500 m^2/g specific surface area). Strategies include (1) increasing hydrogen affinity relative to surface area and (2) using x-ray techniques to study oxidation state and solvation changes to better understand the activation process at the metal center. Reducing synthetic steps for precursors will help keep costs low.



Question 1: Approach to performing the work

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

- The goal of surpassing Chahine's rule for hydrogen uptake is a valid one and would be helpful to the Hydrogen and Fuel Cells Program if it were to be accomplished.
- The principal investigator (PI) has an excellent background in the development of new framework materials for gas sorption. However, the effort, not the approach, seems to be lacking in this project. The slide on barriers was not done correctly; these are not the DOE-defined barriers but the PI's interpretation of barriers.
- The approach to improving on the Chahine rule is reasonable, and MOFs are a good candidate for achieving the DOE goals. PCN-250 might be a reasonable choice for cryogenic adsorption, given its stability. The use of x-ray absorption near edge structures (XANES) might not be the most useful way to determine the degassing temperature, but the project has some results that should correlate with laboratory techniques (though the project team has not attempted to show this comparison). Using both Mossbauer and extended x-ray absorption fine structures (EXAFS)/XANES to characterize the Fe changes with activation is reasonably attempted. The reasoning behind the changes in oxidation state appears to be secondary to actually proving that there is an increased adsorption enthalpy upon oxidation change. There are several high oxidation state MOFs in the literature, and none has shown a large increase in adsorption enthalpy; the MOF-74-$Fe^{2+/3+}$ change, in particular, showed only a small difference (Long, Dalton Transactions).
- Targets and challenges are well defined, but the scientific hypotheses for addressing them are not clear. Increasing the number of strong binding sites, optimizing the pore dimensions, and improving the effectiveness of activation are worthy objectives but not scientific strategies. All three of these are well-known objectives for MOF-based sorbents. The project appears to be focused entirely on improving the gas uptake of PCN-250. The primary objective is to get the uptake to be ≥6.75 wt.%—clarify whether this is excess or total—at 40 bar. The best so far is 4.8 wt.% excess. The goals are very ambitious, but strategies beyond PCN-250 are not clearly defined.
- The approach to addressing the problem of high uptake has been articulated in principle, but there is no adequate description of why this particular open metal site structure is suitable as a hydrogen storage

medium. The project should articulate what the potential energy contours show, how they were calculated, and why they are relevant. There appears to be no significant charge redistribution on the basis of the image shown on slide 8. If this is the case, then a high initial Henry's law enthalpy will be seen in the vicinity of the open metal site, but once that site is occupied, the enthalpy will decrease to values similar to any normal carbon. Fe has an atomic mass of 56, and hydrogen has an atomic mass of 2. The project should define the strategy that will ultimately provide insight that suggests that this particular structure will form the basis of a suitable sorbent.

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

This project was rated **1.7** for its accomplishments and progress.

- Detailed XANES investigation of the activation process was performed. Results suggest that the structure of MOF begins to degrade as temperature is increased. It appears this happens almost immediately as the temperature is raised above room temperature. Removal of the OH group coordinated to iron in the framework requires reducing the oxidation state. This might be possible by adjusting activation conditions, based on Mossbauer data. A systematic investigation of changing the oxidation state of the framework Fe^{3+} to Fe^{2+} is underway.
- So far, there are no strong results related to DOE goals beyond what has been conceptualized and published in the literature.
- The claim of a gravimetric uptake greater than expected on the basis of surface area should have been the basis for this presentation. It appears that no effort was made to understand how this was possible. The first thing that should have been done was to perform a D_2-based neutron diffraction experiment to understand the phenomenon. In the past, understanding higher-than-expected uptake would prompt a serious effort to identify and understand the observation. This does not seem to have happened with this material. The discrepancy between the initial uptake determined by the PI and the difference measured by the National Renewable Energy Laboratory (NREL) was not adequately addressed. The team needs to describe where the initial measurement was done, why those data were not shown, and why there was no explanation given as to the difference in measurements.
  - Figure 10 shows XANES data—a simple density functional theory calculation based on the expected densities of states should have also been performed. The drop in intensity that is stated in the slide is not obvious. Even if it is significant, the XANES peak appears to continue to drop with temperature, without attribution as to why. Slide 11 shows the radial distribution functions (RDFs) of the Fe peak—the rationale for this analysis should be explained. While it is understood that EXAFS provides coordination data, no analysis was done, and again, all we see is a continuing decrease in peak intensity. Slide 13 shows Fe Mossbauer data from a dobdc structure. This is revisiting a system that has been synthesized before; the project should discuss to what end this work was performed. It is already clear that while MOF-74-type structures are interesting, as they show H_2 distances closer than expected, the rationale for this effort was not articulated.
  - Figure 15 shows the results of compression. Since a compression load is indicated, pressure data should be included. The force data give absolutely no idea as to the pressure that the sample can tolerate, which will depend on die size. The surface area of the material used here is lower than the 1600 m^2/g that was presumably measured earlier. Such an inconsistency in specific surface area (SSA) needs to be reconciled. The data as presented on this slide are of no value or meaning at all.
- It was very disappointing to see the incompleteness of the effort; however, even worse was the extrapolation of apparent preliminary work to such broad-based conclusions and implications. How the density was calculated, as explained by the PI, appeared to be wrong. While it appears that NREL did show a sorption that was greater than Chahine's rule, the reasons for this are many. Not all solvent was removed for BET analysis. Long showed how he determined all solvent was removed with infrared spectra; it is suggested that Zhou's group follow suit. Gennett showed how an 8 m^2/g material absorbed ten times Chahine's rule, but seemed to suggest there was a pore structure/volume that could not be accessed from N_2 BET measurements. The PI has the capability to do CO_2 BET measurements with all of his previous CO_2 work. It would be interesting to see the pore volume of this material for the CO_2 measurement. The go/no-go milestone was not achieved. The compaction calculation also appears to be misleading. Also—if one looks at slide 15, figure B—it is interesting how, after degas, the density decreases by 35%. It leads one to

believe there is a considerable amount of solvent in the materials. Slide 15 appears to be a misrepresentation of results; it assumes a direct correlation between the packing efficiency and the capacities. The work of Veenstra in the engineering center on MOF-5 shows this. It is strongly suggested that these pellets be tested for hydrogen uptake *before* claims of packing efficiency can be evaluated.

- The first go/no-go milestone was not met. The goal was to achieve 6.75 wt.% excess, whereas only 4.8 wt.% was measured by NREL.

Question 3: Collaboration and coordination with other institutions

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

- There seems to be reasonable collaboration between Argonne National Laboratory (ANL) and Texas A&M University; samples have also been sent to NREL for verification.
- Collaboration with Carnegie Mellon for Mossbauer is underway, as are x-ray studies at ANL. The project needs to state explicitly whether they are at the synchrotron light source—the presentation does not say. The purpose of the atomic layer deposition studies at ANL should be defined. Slide 18 (Remaining Challenges) says that Texas A&M University investigators will “cooperate with other research groups and institutes to confirm the repeatability and recyclability of PCN-250 in hydrogen storage,” but no specifics are provided.
- The interaction with ANL and NREL should be tied.
- The existing collaboration with ANL does not appear to have produced anything. The XANES work was presumably performed there, but no scientific insight was presented, other than to probe for desorption of dangling components or solvents. Neutron scattering would help this project tremendously and should be a top priority.
- The project team seems to be working with ANL and has sent some samples to NREL, but collaboration seems to be weak.

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

This project was rated **2.2** for its relevance/potential impact.

- If this works, it might be useful. The real issue is the focus at 77 K in that it cannot meet DOE goals.
- It was disappointing—considering the past efforts of the PI—that such claims were made without any data to back them up. The potential impact is outstanding; however, the information as presented is not.
- No clear goal has been articulated. While it is understood that materials development is a difficult task, there are certain physical principles that have not been laid out that describe the strategy that will improve volumetric or gravimetric density. The analytical methods sidestep any real attempt to understand the behavior of the materials that are being developed, and it is not clear that any progress from this effort is actually aimed at addressing programmatic issues.
- The objective of increasing the excess uptake of PCN-250 to a value nearly double that predicted by Chahine’s rule by using metal ion reduction to remove coordinated anions could have a significant impact on the field, if accomplished. However, the presentation does not indicate what the theoretical maximum excess capacity is expected to be, so it is not possible based on the information provided to determine what the potential impact will be. However, the best experimental number at this point is 4.8 wt.%, and the project missed its target milestone of 6.75 wt.%, so it is unclear by what means the ultimate goal of >9 wt.% excess uptake will be achieved for even one MOF, much less the 5+ specified in the Quarter 7 milestone.

Question 5: Proposed future work

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

- Improving adsorption enthalpies and making new materials for Milestones 2 and 3 are excellent goals, but a priority needs to be on sample reproduction ability and experimental capabilities.
- Slide 18 lists vague directions for this effort, which is tied to a single material, PCN-250. Unfortunately, almost nothing has been suggested here that offers a motivation or vision of the particulars of this material. The PI did not present volume density data on this material and, in general, seems totally unengaged with the needs of this project in addressing the physical attributes of a suitable sorbent. It is not clear that the PI has contacted groups in a position to clarify the phenomena he has observed, and the experimental routes he has suggested do nothing to address project goals.
- The proposed work (slide 19) is cast in an aspirational way, rather than stating what work specifically will be done. Beyond PCN-250, no other MOFs are mentioned, so it is simply unclear how this will be accomplished.
- The project should clarify why it is to continue if a go/no-go decision was not reached.
- Having missed the first go/no-go milestone, it is unclear how much extra effort should be devoted to PCN-250.

Project strengths:

- The project PI is one of the top people in the MOF field and has all of the resources necessary to perform the work required by the project milestones. The collaborations appear strong as well and are providing useful information.
- Discovery of new, high-performing hydrogen adsorbents is an important objective. A successful outcome would clearly aid the development of low-cost hydrogen storage systems.
- The PI and the materials proposed are project strengths.

Project weaknesses:

- Specific details concerning the strategies for producing MOF sorbents with excess capacities well above those predicted by Chahine’s rule are not spelled out.
- The PI does not appear to have any interest in establishing the phenomena responsible for the observed uptake in a cogent way so that physical principles can be developed that can be used to better design an adsorbent. The PI was evasive in his answers to reviewers and never fully explained the discrepancies or rationale for the analytical approach used on this material.
- Greater accuracy is requested in future presentations. The PI should check some of the assumed data. Slide 5 has images of supposed packing densities. Solid para hydrogen in the hexagonal close-packed form has a nearest-neighbor distance of 3.793 Å (the lattice constant at 4 K, by Keesom in 1930), but there is variation if there is an ortho-para mix. This solid distance is larger than the calculated Lennard-Jones potential minimum, and larger than that observed in the liquid (neutron scattering and simulation ~3.7 Å). Generating pellets of MOFs is not a useful step at this point given how variable the samples/experimental techniques are for this group. These issues need to be fixed before spending time on projects that will need to be repeated. The PI indicated that the pellet density was determined by immersion in water—clearly this is not a useful way to do that. The PI should review the data and processes in the laboratories to be aware of what is happening. More attention should be placed on understanding the RDF of the activated product, as a rather large second coordination shell at 2.3 Å seems to be growing after activation and cooling. The MOF-74-Fe Mossbauer data was published by the Long group—it is not clear why the data are included here. Relevant material would be better.
- The lack of effort and attention to detail are project weaknesses.
- Missing the first go/no-go milestone is a major concern.

Recommendations for additions/deletions to project scope:

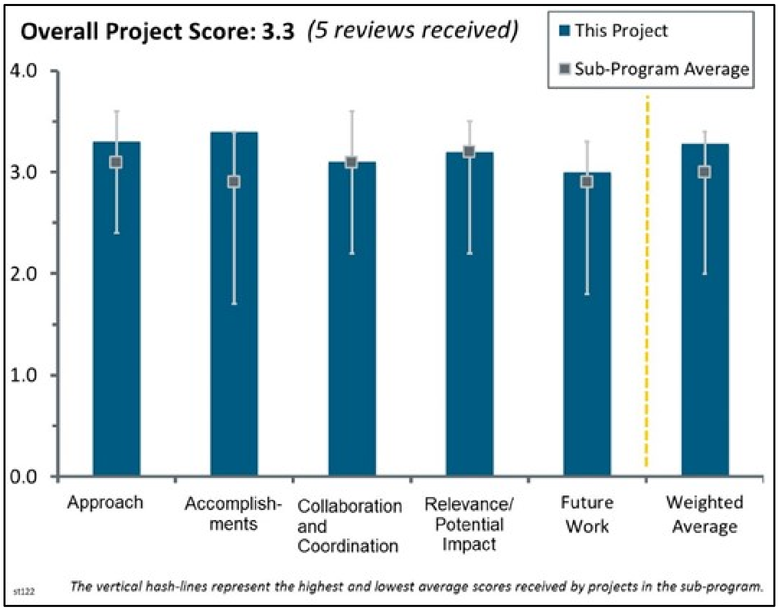
- For future evaluations, the project needs to explain the strategies that are being evaluated for designing new MOFs with the requisite properties. Predictions of the maximum excess uptake achievable for the proposed structures are needed to determine whether the end-of-project goals are achievable.
- The project should work with DOE and NREL to ensure adsorption capabilities are on a par with other laboratories. The project should ensure sample variability is at a minimum. Hydrogen adsorption isotherms should be measured as soon as possible.
- The work on PCN-250 should be scaled back. A clear plan for identifying adsorbents that exceed the Chahine rule by 50% is needed.
- This project appears to have missed the initial milestone of reproducing the results that were claimed in the proposal. This brings the credibility of other results from this project into question.

Project #ST-122: Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections

Don Siegel; University of Michigan

Brief Summary of Project:

A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles. Storage via adsorption is a promising approach, but high gravimetric densities typically come at the expense of volumetric density. This project's goal is to demonstrate best-in-class metal–organic frameworks (MOFs) that achieve high volumetric and gravimetric hydrogen densities simultaneously, while maintaining reversibility and fast kinetics. The approach entails high-throughput screening coupled with experimental synthesis, activation, and characterization.



Question 1: Approach to performing the work

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

- There is nice integration of synthesis, theory, and characterization. The project is using supercritical CO_2 to maximize surface area (trying to get to 90% of the projected area). System-level projections are also underway, in collaboration with the Hydrogen Storage Engineering Center of Excellence (HSECoE).
- As an extension of what the team was doing in the HSECoE, this is logical and well executed.
- The project has a systematic approach using numerically efficient tools. The approach to calculate uptake could be improved; results are specific to one temperature. Results obtained using a classical parameterization of the hydrogen–hydrogen interaction are not really relevant.
- It is an interesting project: evaluating the possible outliers in the framework database for possible improvements to achieve theoretical limits. The principal investigator (PI) does need to gain access to the Materials Genome Initiative database.
- The basis for this effort is shown on slide 8, but the data here bring into question the approach adopted to justify some of the materials that are being studied. In general, a linear dependence on uptake with surface area has not been observed, leading to problem data points such as SNU-21, which has a volume uptake comparable to liquid hydrogen. This was an unphysical data point that required some reanalysis and justification for this part of the presentation. Determining a relationship that optimizes how uptake is influenced by the surface-to-volume ratio would be illuminating for this effort and would suggest physical properties that should be pursued or optimized for uptake, allowing the project to rely less on a data-mining effort.

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.

- Codes for doing computational screening were updated. Grand canonical Monte Carlo (GCMC) is being used to predict adsorption isotherms. The project identified an improved force field that gives greater fidelity to experiments. A large number of MOFs (>2000) were screened computationally to identify structures with the desired capacities. This identified a large number of MOFs that could exceed MOF-5 uptake, in some cases by large amounts. Seven MOFs were identified that could potentially surpass MOF-5 by 15%. A much larger computational screening effort is underway, which would consider >50,000 new materials from the Cambridge Crystallographic Data Centre. The initial go/no-go was met; IRMOF-20 was identified and exceeds the MOF-5 benchmark. A number of other MOFs that were predicted to be promising could not be synthesized with high surface areas according to literature procedures (this is not uncommon). Supercritical CO_2 activation experiments show that this method delivers superior properties (higher surface areas) than the standard vacuum activation; in some cases, the differences are huge (e.g., UMCM-9), so this is an important result. A new database was developed (MOF Dashboard) to track progress on promising materials.

- The project has done excellent work to put the idea of some materials to rest, while others deserve more investigation. The accomplishments were limited only because the PI did not access the Materials Genome Initiative database. It appeared that, by the end of the presentation questions, he was made aware and will access the database in future efforts.
- Identifying optimal mass and volumetric parameters through computational screening, then targeting those materials with a feedback loop to avoid overlooking materials that may be more difficult to activate than others, is efficient. The project has at least one success story in unearthing an overlooked MOF that shows promise. It would be better if these were for room-temperature storage.
- The force field approach seems to do a reasonable job of modeling isotherm behavior. Slide 17 indicates that “intuition” was used to identify compounds of interest. It is not clear what this means. The data on slide 20 indicate that some improvement to gravimetric capacity was calculated, but the volumetric capacities are similar. Because of the larger size of the unit cell, the question is whether this ultimately indicates that a larger “tank” would be required to take advantage of the higher gravimetric uptake.
- Proof of concept is achieved. Other selection criteria could be included.

Question 3: Collaboration and coordination with other institutions

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

- Collaborations are good. Synthesis and modeling are done within the University of Michigan by separate investigators. Ford is a subcontractor doing pressure–composition isotherm measurements, scale-up, and characterization. These appear to be well integrated within the project. An unfunded collaboration with the HSECoE is also underway to assist in development of system models.
- Given the amount of computational screening and characterization that goes on with the Materials Genome Initiative, the project should be working across DOE-funded laboratories to ensure minimal redundancy. There are some known efforts run by Basic Energy Sciences (BES) in this area that have external facing prescience for databases. The collaborators do work well among themselves. The system-level model is understandably a bit absent, given the youthful nature of the project.

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

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

- The project is striving to achieve both high volumetric and gravimetric capacities, which is rare in MOFs (or sorbents in general). The goal is to find a MOF that exceeds the performance of MOF-5 (used as a benchmark). Emphasis is still on cryogenic storage, however, so even if the project is successful, the resulting material will not meet DOE targets regarding storage temperature.
- The combination of theory and experiment is working well and can address some DOE goals. It would be useful, however, if the efforts can be used to scale up the temperature of operation.
- The project is identifying materials that show improvements over MOF-5.

Question 5: Proposed future work

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

- Proposed future work is in line with the goals of the project. However, the project would have a larger impact if the screening could take into account more than surface area. It is clear that open coordination sites on MOFs are needed to get heats of adsorption to the point at which room temperature (or at least some temperature above 77 K) is feasible.
- Also of interest is the nature of adsorption enthalpies in materials of this type. While a modified form of a universal force field is used within a Lennard–Jones type 6-12 model, it is not clear whether the computational effort will provide insights on the isosteric enthalpies of the systems being pursued, although given the closeness of fit, some evaluation of enthalpies would be of value.
- Future work was clearly presented, but it would be good to see efforts to move to higher temperatures.
- The future efforts should include the extended database, so milestones may need to be altered slightly.

Project strengths:

- The team is excellent, with deep experience in all areas needed to perform the project. There are good connections with original equipment manufacturers, and the PI is very cognizant of the practical issues associated with solid-state storage.
- The project offers a possible pathway to a high-throughput evaluation of candidate materials.
- This is a comprehensive, logical, and well-executed project. This is nice work overall.
- The PI team and the completeness of the effort are strengths.

Project weaknesses:

- There are no serious weaknesses in terms of the way the project was originally structured, with the focus on cryogenic storage.
- The project may suffer from duplication of effort compared to other DOE-funded projects in BES. This is easily solvable and might generate some efficiencies by sharing code/platforms, if possible.
- Integration of chemical stability, specific heat, and thermal conductivity requirements are weaknesses.
- Lack of information on other databases is a weakness.

Recommendations for additions/deletions to project scope:

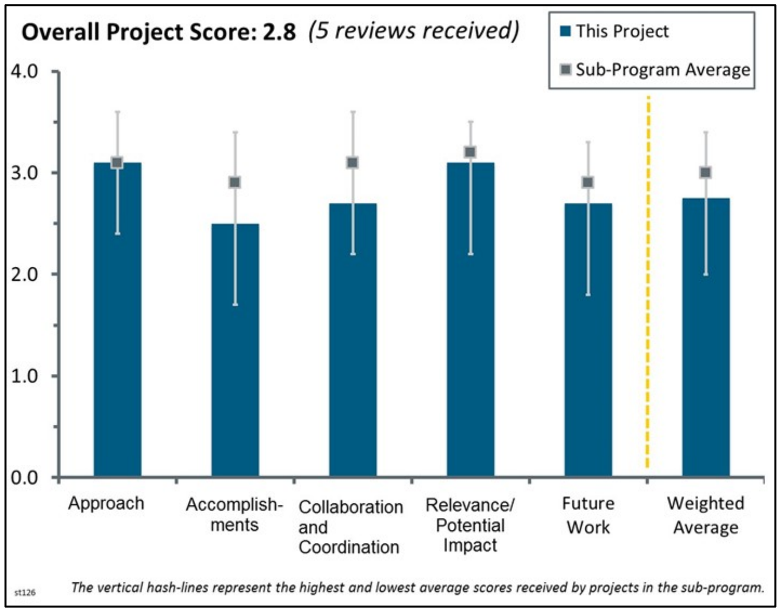
- Taking the possible higher adsorption enthalpies of open metal sites into account in the screening would be valuable. Even though these are difficult to model from first principles, perhaps some empirical relationship could be implemented until more accurate potential energy curves can be incorporated into the force fields.
- The project should target higher-temperature solutions.

Project #ST-126: Conformable Hydrogen Storage Coil Reservoir

Erik Bigelow; Center for Transportation and the Environment

Brief Summary of Project:

The project goal is to develop storage for compressed hydrogen gas that will provide a cost-effective and conformable storage solution for hydrogen vehicles, thereby reducing the cost, weight, and difficult fit of conventional hydrogen tanks. The target is conformable, lightweight 700 bar gaseous hydrogen storage with around 10% gravimetric capacity. Researchers are aiming for continuous production processes for a storage system that can be extended, once proven at smaller sizes.



Question 1: Approach to performing the work

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

- This is an excellent approach to maximize the weight percentage of hydrogen in high-pressure compressed tanks and allow for conformable efficient storage.
- This novel approach has great potential for a preferred method of hydrogen storage for transportation.
- The overall approach for the project is focused on the main barriers for this technology related to the hydrogen permeation, fill temperature limits, and process compatibility. It should be noted that the hydrogen permeation target is incorrect because it is based on the loss of useable hydrogen rather than the permeation value in the industry standards, which is lower. In addition, the project should emphasize evaluating failure modes, such as the evaluation of the burst pressure in the conformable configuration.
- There is a good deal of current emphasis on demonstrating current compressed natural gas (CNG) vessels, presumably with the identified low-permeability liner material. The value of extensive testing at pressures substantially lower than the 700 bar target is not clear. In addition, it does not seem that the possible qualification of these pressure vessels for automotive applications is being considered in any way. Given that the vessels are expected to leak rather than undergo a catastrophic failure, the safety ramifications of these leaks should be considered.
- The approach of developing coiled reservoirs for hydrogen storage is a novel idea, but the presentation does not give a coherent approach to achieving this—only unfounded claims of 10 wt.% with a system mass of 50 kg. The materials presented to withstand such high pressure (700 bar), such as a Kevlar® overwrap and resin-based liner, do not equate. There is no basis for such claims. No data were presented on the composite strength or to show that the resin could possibly support load-sharing.

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

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

- The manufacturing approach is maturing and shows low cost potential. The tank design with liner and overwrap also shows promise.
- The accomplishments are good, although more progress was to be expected for a design that has been previously developed for CNG and other applications. Also, the Accomplishments slides did not mention

any progress with quantifying the main objectives for the project, which are the ~10% gravimetric capacity and cost reductions.
- The progress toward a proof of concept has been slow. At this point, only the resin selection and tooling have been completed, despite the fact that the project is due to end by March 2017.
- Considering the fact that this project started in August 2015, the spend rate seems very low. The project will not progress quickly enough to end on time. More specifically, it is not clear what the value is of developing a test vessel for 5,000 psi when the target pressure for the vessel is 10,000 psi. Presumably, this is related to the fact that the vessels are supposed to leak rather than fail catastrophically. However, this is not necessarily the case. It seems all high-pressure testing is planned to occur at the National Renewable Energy Laboratory (NREL). There seems to be no coherent plan beyond testing based on the current CNG vessel configurations. If there is a plan, it was not communicated well.
- No data were presented except for some initial modeling data on the thermodynamics of refilling. There were many pictures of the corrugated molding device and Kevlar spooling, but there was no material performance or cost data to show that this is a viable option. Presumably no real accomplishments have been made on this project toward meeting the goal of demonstrating a 700 bar tank that meets the hydrogen storage technical targets nor the stated 10 wt.% storage target listed in the presentation.

Question 3: Collaboration and coordination with other institutions

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

- The effort to expand the collaboration of the project with NREL, CSA Group, and Kuraray Group is encouraging. The project should further explain the respective roles of the Center for Transportation and the Environment (CTE) and the University of Texas. The manufacturing process partnerships should also be provided because it is uncertain whether High Energy Coil Reservoirs is the producer or the developer of the technology.
- CTE's role appears to be to coordinate and report on this project; outside of that, CTE's role is limited. Unfortunately, during the presentation of progress to date, it came across that there was not a complete understanding of the technology being developed by the other partner organizations. Perhaps co-presenting with partner organizations would help to clarify things.
- Future work should include an original equipment manufacturer end user such as Ford to really drive the design and requirements.
- Collaborators were listed, but their contributions were not clear.
- Until this point, there seems to have been no collaboration with other institutes.

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

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

- The ability to have conformable 700 bar tanks using Kevlar overbraid with extruded liner can ultimately improve the weight percentage of hydrogen, lower the cost of hydrogen tanks, and allow flexibility in installation. Achieving this will get us closer to meeting the DOE cost and density targets.
- The relevance of this project is very high if the tank can achieve a 10% gravimetric capacity and meet the DOE ultimate target. Although it was not emphasized in the project presentation, the development of a conformable 700 bar tank would be a significant contribution to the industry with the assumption of improved volumetric density.
- The project has high potential impact to make hydrogen storage safe, make it affordable, and make it fit with current automotive designs.
- The project concept and goals are excellent. The ability to conform a hydrogen storage tank to an oddly shaped area would indeed be a game-changer. However, there are some key areas that do not appear to be part of the project. One major issue is safety: it does not seem that a vessel that will leak, releasing an extremely flammable gas, is realistically able to be qualified for automotive applications. Type V (linerless)

pressure vessels with conventional shapes have met with much resistance for similar reasons, so there is no reason to think that these vessels would be any different.
- The project has good alignment with DOE objectives, but there is no evidence that it can achieve those objectives.

Question 5: Proposed future work

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

- Task descriptions (i.e., titles) are laid out in a way that makes sense. However, it did not seem like details beyond the Task 1 go/no-go decision point have really been considered. Given that it seems that the project might already be behind schedule, having these detailed plans in place would enable a quick push forward assuming that the “go” is given. Safety should be considered as a part of the project.
- A few items, such as resin selection and testing of vessels, were fine, but there was no discussion of materials properties testing. There should be solid materials testing and evaluation prior to moving forward on vessel design and testing. There is no efficient feedback mechanism to understand materials properties.
- The work plan is rational and sound. Durability of the dry Kevlar braid as a function of road vibration is a concern. The project needs to include an automotive company to develop possible other showstopper tests.
- The future work description is effective in communicating the path forward to develop the technology. The project should also consider conducting a detailed cost analysis to provide information about its claims about achieving results near the ultimate cost target.
- The proposed work is focused on implementing a proof of concept. However, the proposed work lacks risk management plans, should challenges be encountered. For example, if the tanks are to fail the high-pressure tests, then thicker walls/other materials will be needed, translating to much lower weight percentage and higher costs, which could negate the advantage of the concept.

Project strengths:

- The idea of conformable hydrogen storage is a game-changer, allowing efficient usage of in-vehicle space.
- The novel approach shows great promise to reduce cost and achieve novel geometry to save trunk space.
- The strength of the project is the game-changing approach to store compressed hydrogen with a conformable solution.
- Strengths include the presence of existing technology and know-how to produce the proposed tank.

Project weaknesses:

- The weakness of the project is the lack of understanding regarding industry standards and analysis of failure modes associated with the technology. The project does not have any activities associated with cost analysis of the design. The concept utilizes a dry fiber without resin, which has a benefit for weight and cost but may not be practical over the life of the pressure vessel.
- Limited data are available to date on hydrogen permeability of polymer liner materials. If the permeability is not sufficiently low, the technology will not be useful. Safety—i.e., why leaking hydrogen is acceptable—is not addressed at all. There may be regulatory hurdles that are virtually insurmountable.
- The project needs to fully understand durability requirements and evaluate accordingly. Kevlar strength reduction as a result of vibration-induced abrasion is a known issue. It may be possible to overcome this issue through proper sizing.
- Weaknesses include absence of any preliminary proof of concept and also of a risk management plan to maximize the project’s odds of success.

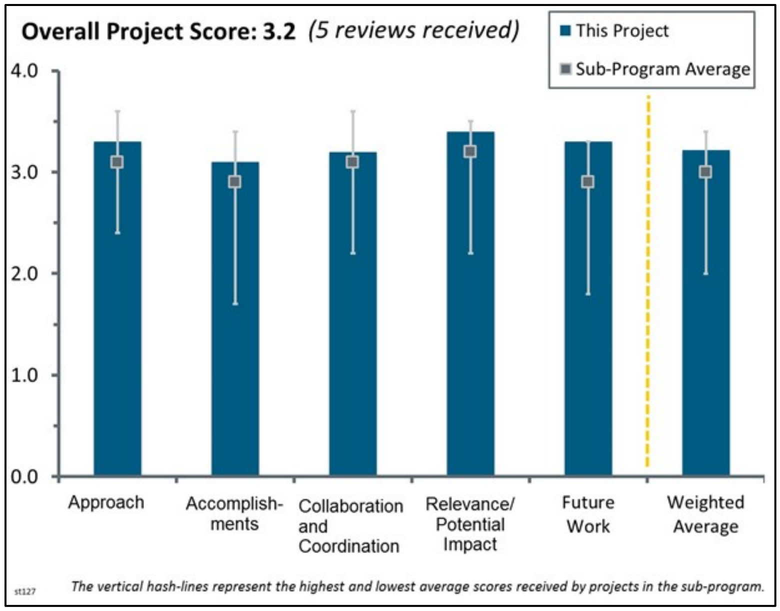
Recommendations for additions/deletions to project scope:

- The recommendations for this project are to revise the permeation criteria, include cost analysis at an early stage, and evaluate potential failure modes in respect to the certification and application. In addition, the project should highlight the benefits of the conformable technology for improvements in volumetric density in a practical vehicle package.

- Given the technical hurdles that may face this project, risk management plans using engineering trade-off solutions are needed in order to evaluate this concept's viability and potential. For example, if the tank wall needs to be thicker, then the project should determine how thick and how this relates to the weight percentage and cost, etc.
- The project needs to fully understand durability requirements and evaluate accordingly. Kevlar strength reduction as a result of vibration-induced abrasion is a known issue. It may be possible to overcome this issue through proper sizing.
- It would be good to see safety and regulatory concerns added to the project scope. There is no path forward to a commercial product if these are not addressed in conjunction with technology demonstration.

Project #ST-127: Hydrogen Materials–Advanced Research Consortium (HyMARC): A Consortium for Advancing Solid-State Hydrogen Storage Materials

Mark Allendorf; Sandia National Laboratories



Brief Summary of Project:

Critical scientific roadblocks must be overcome to accelerate materials discovery for vehicular hydrogen storage. The project objective is to accelerate discovery of breakthrough storage materials by providing capabilities and foundational understanding. Capabilities will include computational models and databases, new characterization tools and methods, and customizable synthetic platforms. Foundational understanding is needed for phenomena governing the thermodynamics and kinetics limiting development of solid-state hydrogen storage materials.

Question 1: Approach to performing the work

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

- This effort focuses on developing computational and experimental methods that enable and accelerate materials discovery. A straightforward and well-thought-out approach has been formulated that starts with validation of models and experimental tools using well-understood systems, followed by a rapid progression to understanding thermodynamics, reaction mechanisms, and structural transformations in more complex materials that show promise of meeting U.S. Department of Energy (DOE) goals. The approach is deliberate and logical. The approach focuses on development of advanced computational models and databases, improved characterization tools, and tailorable synthetic platforms. An important element of the overall approach is ultimately to make these advanced capabilities available to the hydrogen storage research and development (R&D) community. Assuming that a timely progression to more complex materials occurs, the approach should provide a solid foundation for achieving steady and meaningful progress.
- This is an excellent research consortium seeking to address systematically fundamental issues about solid-state storage.
- HyMARC's approach represents a "reboot" in the thinking about developing viable materials-based storage approaches. As the "traditional" make-it-and-test-it approach has not yet yielded a material that can attain all of the DOE hydrogen storage target properties, HyMARC's new approach is to develop a computational basis for understanding and developing the enabling foundational science of the key controlling features of hydrogen storage materials. Along the way, new characterization and synthetic tools will be developed to experimentally test some of the key strategies uncovered by modeling. The approach is focused on what many believe are the key barriers: achieving higher heats of sorption in sorbents and achieving vastly improved kinetics of dehydrogenation/rehydrogenation of complex hydrides. Both are problems that have not succumbed to the make-it-and-test-it approach. Developing the enabling methods, and not the materials, represents an innovative, high-risk approach with a large potential benefit if the project succeeds. Where the approach can be improved lies in quickly selecting the "best" prototype systems to answer the key questions, and being prepared to shed materials and redirect efforts that are not in line with achieving HyMARC/DOE goals as quickly as possible. This will largely be a management judgment issue. The choice of working on graphene nanobelts and Lewis acid zeolites was not well supported. It is not clear

how these are leading to useful prototype materials to support the theory, modeling, and characterization focal points.

- The proposed work takes on a "six-task" approach that is logical (and does not appear to miss any major categories). The work is inclusive of all types of hydrogen storage materials: sorbents, hydrides, and liquids. The overall strategy is to begin with materials that are well studied, such as $NaAlH_4$ and MgH_2. Although these materials have been well studied, HyMARC's role is for this team to develop new techniques and approaches. Validation of those techniques using well-studied systems is a logical approach. Two new techniques are low-energy ion scattering (LEIS) surface observation of hydrogen atoms (available only at Sandia National Laboratory [SNL]) and 3 nm ptychography at beamlines. The selection of $Mg(BH_4)_2$ comes from the desire to utilize the Characterization and Validation team to demonstrate the entire team's capabilities. This is a worthwhile objective. There is also a weakness: The proposers intend to examine complex systems such as nanostructured hydrides within graphene nanobelts. The proposers should provide a better explanation for the path of materials selection—why graphene nanobelts are chosen over other forms of graphene.
- It is not clear how data mining as described during the presentation is to benefit solving the storage problem. The following questions arise: what specific information is to be gleaned from this effort, whether nanoscale synthesis is a route that makes sense, and what is to be learned that has ultimate engineering applicability. Nanoscale materials presumably have a large surface energy component, and nature will work to reduce surface free energies via grain or particle growth. While this may contribute to aid in solid-state diffusion, which is the bane of complex hydrides, it seems that an approach that isolates surface facets would offer less ambiguous technical and scientific data. It is not clear how good the computational tools will be in ultimately developing engineering materials. It is not clear that there are any examples of a computational approach predicting the engineering performance of a new material.

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

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

- The HyMARC effort is off to a good start. The project comprises six inter-related tasks that comprehensively address the important challenges facing the development of high-capacity hydrogen storage solid-state materials commensurate with practical fuel cell applications. Preliminary data using LEIS (a unique and particularly promising diagnostic tool) and in situ soft x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and x-ray emission spectroscopy (XES) characterization methods are encouraging. Likewise, impressive initial results from the computation and theory effort are providing confidence that a more rigorous and comprehensive understanding of the primary thermodynamic and kinetic effects that control sorption reactions in increasingly complex systems will be forthcoming. Work on size control for complex hydrides and creation of a nanoparticle library for a prototype hydride material is in progress, and that should provide a means for evaluating nanoscale engineering approaches for enhancing sorption kinetics.
- It is likely a little early to have much of a discussion about progress on accomplishments for HyMARC, as the project is still in start-up mode. Access to various characterization tools is being ironed out, theorists are benchmarking computational models, etc., but it is early in the project, and things appear to be going well. The project appears well managed at this point, and the team that has been put together is technically very strong.
- The project has existed for less than one year. In this time, the proposers have achieved the following: two publications, three years of beam time for multiple beamlines, post-doctorate hiring from Princeton, hiring from the Massachusetts Institute of Technology and Dalhousie, and approval of user proposals.
- On slide 13, several different key results are noted. It would be good to know what paper is under review and what the results are that are not part of the manuscript. On slide 14, while hydrogen diffusion has been cited, it seems that diffusion of other species in complex hydrides is the actual problem. The relevance of hydrogen diffusion through alumina that was mentioned in the presentation is unclear. The project has just started, so it is difficult to gauge the utility of the tools that are being developed and how they will be used by the community at large. As the project has just started, accomplishments are limited to hiring people; presentation of actual data was limited.

- The reviewer agrees with the overall approach. Progress is as expected for a consortium that ambitious. The project should probably address more clearly why the materials to model were selected.

Question 3: Collaboration and coordination with other institutions

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

- Effective use of collaboration is evident. The Molecular Foundry and Advanced Light Source (ALS) are being accessed through a user program (with an increased amount of time). Computing at the Molecular Foundry and SNL permits multiscale computational models. Large team interactions are ongoing, with meetings occurring along the lines of tasks (on a regular basis). This is a well-designed construct for interactions. Many team members are co-located in the San Francisco Bay area. Face-to-face meetings can be used to enhance excitement among graduate students and postdocs—the project should take care not to examine a singular problem but to take a broad approach to ensure that the materials problem is being addressed. Regarding weaknesses, it would be useful to have a quantification of meetings; the description “on a regular basis” is too vague.
- Development of a framework that enables and facilitates effective collaboration among the many HyMARC participants is a critical management challenge. A robust organization structure is in place, and thus far, good coordination among activities and researchers in most of the six tasks is evident. Although the work being conducted on the companion consortium led by the National Renewable Energy Laboratory (NREL) directly complements the HyMARC activity, closer coordination between those two efforts will be essential to avoid duplication and to ensure that the “right” problems are being addressed. The challenge will become even more daunting as new participants are added to the HyMARC program. It will be critical for project management to address those challenges in a serious and focused way.
- The success of HyMARC will in large part depend on how well the team members collaborate among themselves and with the hydrogen storage community at large. So far, all appears to be going very well. They have clearly learned a good deal from watching the other Centers and appreciate the “Center Concept,” in which collaboration is crucial to success. A key metric for how the collaborations are coming along in the future will be assessing how HyMARC has come together as a team to prioritize efforts and resources to most rapidly answer the key questions, as well as to redirect lagging efforts. It currently appears that appropriate collaborations outside of HyMARC are coming along nicely.
- The list of collaborators is large. The budget is rather limited, and so the degree of commitment by each of the members is unclear. The physical proximity of the laboratories is good, and being in the same time zone is good, but it is not clear how well geographic proximity reduces the activation barrier to communication, especially given the overlap of slides shown by partner laboratories.
- It is difficult to judge at this stage, as the project is new. The project should make sure to coordinate with other ongoing projects.

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

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

- This project has the potential to be a “game changer” for DOE. Although prior efforts and activities in individual projects and in the materials centers of excellence provided useful results that had impacts on new materials discovery, that information was largely heuristic and phenomenological. The HyMARC project provides, for the first time, an R&D framework devoted solely to development of experimental and theoretical techniques that can be used to understand the fundamental kinetic processes and thermodynamic properties that enable new materials discovery and development. If successful, this could be a truly impactful project for DOE.
- Developing the foundational science to better understand, for example, the origin of the kinetics barriers in complex hydrides may be key in developing next-generation materials that can meet all of the targets. This is clearly highly relevant to DOE’s goals and objectives. If the project succeeds in developing the enabling

science, the multiscale modeling, the characterization tools, etc., that underpin what makes a viable storage material, then this can have a tremendous impact on future hydrogen storage developments.
- Storage is a critical issue. Validating theory and simulation models is necessary at this stage to bridge the perceived gap between experiments and theoretical work.
- The surface science is exceptionally strong and leverages the Basic Energy Sciences program at SNL. Regarding weaknesses, no system should be selected without clearly defining its usefulness in the HyMARC testing and validation schema.
- The overall goal is to help with new principal investigators' projects that emphasize materials development and to help them with analytical/computational tools to which the investigators may not have access.

Question 5: Proposed future work

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

- Future work will initially focus on validation of tools and techniques on systems that are already (fairly) well understood. The intent is to rapidly progress to understanding more complex processes and systems. This overall approach is reasonable and prudent, assuming that the project participants fully understand that a timely transition to more complex systems that could potentially meet DOE goals is essential. It is easy to be lured into detailed studies of interesting processes in "simple" systems that may be largely irrelevant to more complex materials. It seems evident that the HyMARC team understands this distinction and that they will make a straightforward and rapid progression from simple to complex systems as the project evolves in the next year.
- Developing a set of criteria for developing a decision tree or something similar for selection of the optimal prototype materials seems as if it would benefit the library development of prototype materials. This will help the collaboration to also redirect efforts and resources that are not on track to answer the key questions posed to more promising areas that directly support achieving the goals of HyMARC and the technical targets of DOE.
- The database task will begin in year 2. The team has gained ongoing beam time for x-ray studies. This is useful. There are no weaknesses in the proposed future work.
- Perhaps some clarification should be given at the next Annual Merit Review (AMR) about R&D performed on new materials.
- Future work is unclear until new projects are initiated that collaborate with HyMARC.

Project strengths:

- A highly capable team comprising experts in theory/modeling, advanced methods for materials characterization, and materials/structure synthesis have been assembled. Co-location of team resources and facilities should enhance coordination and collaboration in such a large and diverse project. A solid plan is in place to tackle the difficult problems that underlie a detailed understanding of the critical processes operative during sorption reactions in adsorbent media and complex hydride materials.
- The project has strong management and a very strong technical team. The project has a wholly new approach: to circle back to develop the foundational science of storage materials.
- The team is well managed and has quickly organized into sub-teams along the lines of tasks. The team is poised to make advances in discovery for sorbents and hydrides.
- This is an excellent and impressive team.

Project weaknesses:

- It is not apparent that the work of the Lawrence Berkeley National Laboratory (LBNL) team is fully integrated into the overall project. There is concern that the LBNL/ALS group will operate in a semi-autonomous way on materials and advanced diagnostics that may be of special interest to that group but of less relevance to the Office of Energy Efficiency and Renewable Energy. It is incumbent upon the project management to ensure that all efforts are focused on achieving the principal goals of the project and that the overall project is coherent and cohesive. As pointed out at the AMR, it will be important to recognize expeditiously whether information obtained in validation studies on simpler or widely studied systems

(e.g., $NaAlH_4$) will be readily extendable to more complex materials (e.g., $Mg(BH_4)_2$). (It should be noted that this comment should be viewed more as a "caution" than a "weakness.") The project must be sufficiently nimble so that mid-course corrections can be made accordingly. There is a notable lack of advanced nuclear magnetic resonance (NMR) and neutron diffraction capabilities. These diagnostics are essential for a project of this kind. Closer collaboration with the NREL-led consortium and "funding opportunity announcement (FOA) projects" is essential.
- The choice of materials selection should be better explained. With the onboarding of materials system projects, it is important to classify the materials system in relation to HyMARC goals (i.e., some materials are selected because they make a unique testing platform, and others are selected for development as hydrogen storage systems).
- There is a very minor weakness: a justification of the methodologies used or proposed would be appreciated.
- The choice of prototype materials not well developed and is disjointed.

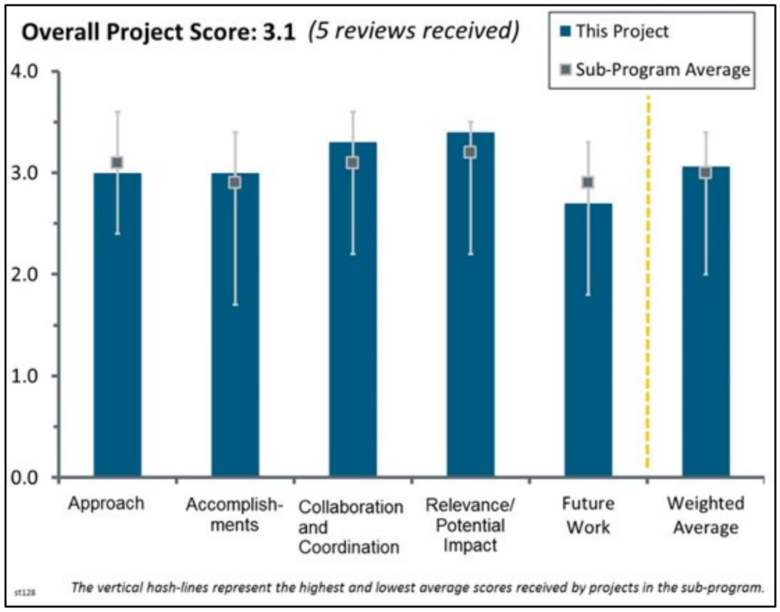
Recommendations for additions/deletions to project scope:

- It may be helpful to bring investigator(s) with more extensive synthetic and mechanistic chemistry expertise into the project. Although an impressive array of theory, modeling, characterization, surface science, and materials development capabilities exists in the project as currently constituted, the involvement of an individual/individuals having deeper "chemical intuition" could be beneficial in making the difficult decisions concerning evolving research directions (especially concerning kinetics and reversibility issues) in the project. Advanced NMR and other "H-centric" diagnostic capabilities, such as neutron diffraction (the National Institute of Standards and Technology), and VISION (Oak Ridge National Laboratory), are needed. This may involve a much closer connection with the NREL consortium and/or the addition of complementary DOE-funded projects that augment the HyMARC effort.
- The explanation of the HyMARC collaborative must be re-stated clearly for the hydrogen storage community to fully understand its role in developing testing and validation platforms (i.e., developing the toolset to improve materials discovery). Since some materials systems must be selected and used for developing test and validation platforms, it is recommended that the team identify the test/validation platform demonstrated by each materials system selected for future review cycles. No system should be selected without clearly defining its usefulness in the testing schema.
- It is unclear how graphene nanobelts and functionalized or otherwise zeolites are going to help HyMARC develop the materials systems that will assist the development of the foundational science of targeted sorbents and complex metal hydrides. It is recommended that HyMARC develop a defensible prototype materials strategy that the storage community at large can accept. That community is presumed to be the future customer of HyMARC output.

Project #ST-128: HyMARC: Sandia National Laboratories Effort

Mark Allendorf; Sandia National Laboratories

Brief Summary of Project:



This project addresses a lack of knowledge about hydrogen physisorption and chemisorption. Researchers will develop foundational understanding of phenomena governing the thermodynamics and kinetics of hydrogen release and uptake in all classes of hydrogen storage materials. Sandia National Laboratories (SNL) will (1) provide data required to develop and validate thermodynamic models of sorbents and metal hydrides, (2) identify the structure, composition, and reactivity of gas–surface and solid–solid hydride surfaces contributing to rate-limiting desorption and uptake, (3) synthesize metal hydrides and sorbents in a variety of formats and develop in situ techniques for their characterization, and (4) apply multiscale codes to discover new materials and new mechanisms of storing hydrogen.

Question 1: Approach to performing the work

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

- This investigation provides details of the SNL specifics with regard to computation (molecular dynamics [MD], density functional theory, and database), experimentation (metal–organic frameworks [MOFs], nano and bulk metal hydrides, and high-pressure synthesis), and characterization (gas sorption, soft x-ray synchrotron, in situ x-ray diffraction, Fourier transfer infrared spectroscopy, and x-ray photoelectron spectroscopy [XPS]). This broad set of experiments will benefit the Hydrogen Materials–Advanced Research Consortium (HyMARC) and those who provide materials for evaluation and validation.
- This project is a critical element of the experimental effort in the HyMARC project. The approach is very expansive—it addresses important issues relevant to hydrogen storage in adsorbents (mainly MOFs and doped carbons) and a wide range of bulk and nanoscale metal hydrides with catalytic additives over an extended pressure range. A suite of characterization instrumentation, mainly surface-sensitive probes, is being employed to study hydrogen sorption reactions at surfaces. The focus is on validation of the approach using well-understood systems, followed by a rapid progression to more complex systems. Although the approach is comprehensive, it seems unlikely that all of the proposed work can be accomplished with the funds and resources allocated for this project. The research and development (R&D) team is strongly encouraged to prioritize the efforts in all of the tasks and to address only those topics that have the most impact for the overall U.S. Department of Energy (DOE) Hydrogen and Fuel Cells Program (the Program). Without this information, it will be difficult to conduct an insightful review of the project approach as it evolves.
- The HyMARC team (and SNL as team lead) has a difficult balance to navigate. The most significant benefit the team brings to the Hydrogen Storage program is the ability to examine the issues that are holding back hydrogen storage, using a complementary suite of techniques and expertise and with a significant amount of effort. Although not a materials development project, HyMARC, of course, must choose materials to examine. The team also has the opportunity to bring new experimental techniques to bear in an effort to shed a new light on problems. The challenge is to keep the primary target in sight and not be sidetracked by materials or technique development unless these are firmly required to understand

issues that will benefit the wider Hydrogen Storage program. The approach in general has been constructed in a reasonable manner; however, some of the experimental techniques give the impression of being utilized more because they are new and available than because they are the best for the purpose. The team needs to keep a watch on this.

- The assortment of state-of-the-art theory, synthesis, and characterization capabilities being developed at SNL for HyMARC clearly has potential to be of value in the development of high-performance, high-capacity hydrogen storage materials. The exception to this is the Li_3N nanoconfinement work, which is something of a recycle of work that has been done elsewhere and seems highly out of place in HyMARC.
- The responsibilities within HyMARC, in terms of validating the modeling activities to provide support with materials preparation, are useful to the overall consortium activities. However, these studies will use only known, although not well-understood, select material systems, all of which are incapable of meeting the DOE targets. The strategy of this project toward meeting the DOE targets ideally needs to go beyond just understand existing materials, such as sodium alanate or magnesium borohydride, to inspiring or driving novel approaches for materials-based storage.

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 research has made developments in solid–solid phase transitions, paying particular attention to minor phases, byproducts, etc., in order to understand and tune reaction pathways. The development of a high-pressure system at SNL is underway to reach 1000 bar. SNL also has a low-energy ion scattering (LEIS) system.
- The upgrading of the high-pressure station and production of the clean transfer holders are excellent, technical, and very important steps forward toward achieving the level of technical excellence envisioned for HyMARC. The establishment that LEIS can be used to study surface hydrogen diffusion is also an important accomplishment. However, the studies—LEIS, XPS, MD calculations, and catalytic additive studies on Ti-doped $NaAlH_4$—seem only to add to the controversy about the fundamental processes occurring in this system and are tangential to the goals of HyMARC. Furthermore, it is surprising that there is no awareness that a large number of studies of Ti-doped $NaAlH_4$ by soft x-ray techniques were reported in the literature many years ago.
- Initial results have been obtained on all five tasks in the project. The work on tracking the surface composition of Ti-doped $NaAlH_4$ during hydrogen desorption is interesting and potentially useful. Moreover, it can be used to validate the utility of the unique LEIS capability at SNL for monitoring surface reactions. However, it will be critical for the R&D team to use that information as a foundation and to rapidly progress to metal hydride systems with volumetric and gravimetric capacities that meet current DOE goals. The ability to explore processes at higher pressures using the upgraded SNL reactor should provide important new information that can be used to guide future work. The relevance of the use of MD simulations to predict H diffusion barriers in Al is puzzling. The relevance of the effort was not clearly motivated in the presentation. Nanoscale effects and nano-interface engineering may prove to be invaluable for overcoming kinetics limitations. Initial results are promising. However, concerns remain about clustering and agglomeration that might ultimately limit reversibility. The effect of surface oxidation on hydrogen sorption reactions was recognized and is being investigated. This may be a critical component of the overall effort. However, surface preparation in an ultra-high vacuum (UHV) environment may be needed to fully assess the role of oxidation. Finally, the MOF studies are important to developing models for adsorption. The participants are strongly encouraged to actively collaborate with researchers in the National Renewable Energy Laboratory (NREL)-led consortium to avoid unnecessary duplication and overlap of efforts.
- These are the early days for the project, so it is difficult to assess, although progress appears good. As has been discussed at meetings with these researchers before, the interpretation of the $Li_3N/LiNH_2$ results may not be “fundamentally altering the reaction path” as suggested. Rather, the importance of surface energies in nanostructured materials means that thermodynamics and, in particular, phase nucleation are altered, which affects the kinetics of the reaction path so that intermediates may not be observed as discrete phases. The team should consider this as it seeks to generalize its findings to other systems.

- The consortium is only few months old, so the project has not made much progress.

Question 3: Collaboration and coordination with other institutions

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

- A large number of external collaborators are involved in the research. The collaborations will strengthen this HyMARC project by providing unique characterization tools and/or insight into relevant material systems.
- SNL and much of the HyMARC team have reached out to other groups to communicate and exchange samples, and early signs are positive with respect to collaboration.
- An extensive network of excellent collaborators has been established. The collaborations need to be better coordinated to enhance productivity and to keep these efforts focused on attaining the overreaching, foundational understanding of hydrogen absorbing materials that is the goal of HyMARC.
- Collaboration with several other institutes was mentioned; however, the direct impact on the current status is not very clear.
- Although solid collaborations with other HyMARC partners are evident, coordination of the work on this project with the Lawrence Berkeley National Laboratory/Advanced Light Source (ALS) HyMARC activities has not been clearly articulated. Close collaboration with the NREL-led consortium will be needed as the project evolves. This will be especially important for the MOFs/adsorbent work. The principal focus of the diagnostic effort in this project is on surface characterization. However, it seems that a more robust activity employing other “H-centric” diagnostic capabilities such as advanced (magic angle spinning) nuclear magnetic resonance (NMR), neutron diffraction and vibrational spectroscopy (e.g., the VISION spectrometer at Oak Ridge National Laboratory [ORNL]) will be needed as the project progresses. Although some of those external collaborations were mentioned (slide 21), the connections with the technical tasks in this project were not described.

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

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

- The project strongly supports Program goals by attempting to identify key factors that may overcome barriers to meeting the storage targets. The potential for progress will become more apparent as the project matures and interacts with other independent projects.
- As a primary component of the HyMARC activity, this project is critical to advancing our knowledge about hydrogen storage in relevant materials. It directly supports Program goals.
- The effort to develop hydrogen storage materials that meet DOE targets has long been in need of improved fundamental understanding of promising new systems. The capabilities being developed by SNL have potential to provide the requisite insights into these systems.
- The work is highly relevant. Particularly, the clean transfer chamber and LEIS system being developed will have a broad impact on hydrogen storage research.
- The ability to experimentally understand fundamental phenomena in select materials and use modeling to predict the performance is useful to the science of hydrogen storage materials. However, it is difficult to envision the impact of these findings on helping meet DOE targets because these findings are likely unique to only these material systems.

Question 5: Proposed future work

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

- The development of an anaerobic interchange is suggested and is a strength. This development will lead to new tools designed for working with individual projects and instruments. There does not seem to be a plan in place to broaden the anaerobic interchange chamber architecture to the wide user community (which may pursue measurements at laboratories other than the ALS and the LEIS system).
- While the plan that relates to the selected materials is clear, the timeframe to achieving thorough experimental understanding of the behavior to precise modeling of these seems to be difficult to meet. In addition, a strategy toward translating these findings and this modeling to other material systems is necessary and is missing.
- Proposed future work is essentially a continuation of current work. There do not appear to be decision points or mitigation strategies in the material presented.
- The future work was addressed only in the most cursory way (slide 18). Consequently, it is difficult to assess the extent to which research priorities and future directions have been established for the project. Because this project encompasses such a broad array of R&D topics and issues, a more complete and compelling description of future work is needed.
- There was nothing about the future research plans in the presentation, and only a few vague remarks were made when the presenter was asked about this during questioning.

Project strengths:

- A strong and exceptionally capable R&D team is conducting the R&D work on this project. Unique and powerful synthesis capabilities (e.g., advanced high-pressure reactor) and surface diagnostic instrumentation (e.g., LEIS) are being used to address critical issues. Solid collaborations within HyMARC and externally are evident. The project is well managed and coordinated.
- The strong team of researchers at SNL has the ability to identify and develop overreaching capabilities for the development of all classes of hydrogen storage materials that were envisioned for HyMARC, such as the upgraded high-pressure facility and the development of the LEIS method for the study of hydrogen diffusion on surfaces.
- The team is competent with a wide range of experimental and computational tools.
- Some focus on foundational aspects of hydrogen interaction with materials that could explain limitations of current storage materials and offer pathways for improvement is a project strength.
- A broad set of tools will benefit HyMARC.

Project weaknesses:

- Some work seems disconnected; for example, the nanostructure investigation remains focused on Li_3N-based materials, while much of the other work is examining $NaAlH_4$. While there is a need to discover general principles, there is also value in characterizing a chosen system from the different aspects being considered.
- Broadened plans are needed, particularly where it pertains to the interchange system being developed. It is not clear whether researchers will have the opportunity to access the design plans in order to modify their instrument. If so, it is not clear how this exchange of information will be managed.
- Although it is necessary to benchmark new equipment and techniques, long-term studies of the old materials should not become all-consuming.
- Based on the project's approach, understanding of the selected known systems does not necessarily extrapolate to other materials. To meet the DOE targets, new ideas and material systems beyond those existing are needed.
- The project has an extremely broad scope, covering a variety of material classes, reaction pressures, structures and sizes, and characterization modalities. Without a more careful prioritization of effort, it is not clear whether real impact on any single topic will be forthcoming. The team is strongly encouraged to thoughtfully evaluate priorities, decide where rapid progression from a simple to more complex system(s) is needed, and look for gaps that can be filled by external collaborations. That information should be

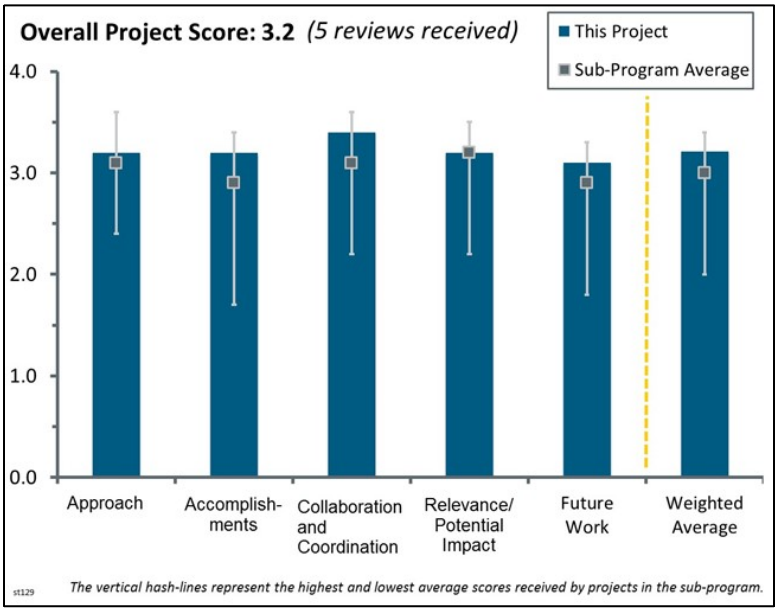
communicated to DOE project management in a timely way so that adjustments in scope can be implemented as needed.

Recommendations for additions/deletions to project scope:

- More robust NMR and neutron diffraction capabilities are clearly needed in the project. Hopefully, funds are available to support collaborations with Pacific Northwest National Laboratory and the National Institute of Standards and Technology so that these tools can be readily utilized. Also, vibrational spectroscopy using neutrons rather than photons (VISION spectrometer at ORNL) could greatly complement the information gained from use of the existing techniques. The role of surface oxidation could be important/dominant in controlling the kinetics of hydrogen sorption reactions. That is well recognized by the project team, and some initial plans are in place to study the effect. However, it does not seem that the stated approach will address the critical issues. The tools that are available to the SNL team are most impressive. If they could be coupled with a UHV reactor with surface-cleaning (e.g., ion sputtering) and oxygen-dosing capabilities, a truly definitive study could be conducted. This is a difficult endeavor that could be an unwanted diversion; however, its importance cannot be overstated. If preliminary work already planned produces results that warrant a more complete study, the team should explore the “UHV option” with DOE management.
- The explanation of HyMARC must be restated clearly for the hydrogen storage community to fully understand its role in developing testing and validation platforms (i.e., developing the toolset to improve materials discovery). Because some materials systems must be selected and used for developing test and validation platforms, the team should identify the test/validation platform demonstrated by each material system selected for future review cycles. No system should be selected without clearly defining its usefulness in the testing schema.
- It would be useful to define material systems/stages in this project with a clear added benefit and milestone for each stage. It is recommended that the team define a strategy for this project and give a clear idea of where it would be heading and how it could help meet the DOE targets.
- It is difficult to make recommendations at this early stage of a far-reaching project, but a greater degree of focus on a critical process among the HyMARC partners could be beneficial.
- The project should suspend all studies of Li_3N and Ti-doped $NaALH_4$.

Project #ST-129: HyMARC: Lawrence Livermore National Laboratory Effort

Brandon Wood; Lawrence Livermore National Laboratory



Brief Summary of Project:

The Hydrogen Materials–Advanced Research Consortium (HyMARC) is providing community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials. HyMARC team member Lawrence Livermore National Laboratory (LLNL) is conducting porous carbon synthesis; x-ray absorption/emission; and multiscale modeling including density functional theory (DFT), ab initio molecular dynamics (AIMD), phase-field mesoscale kinetic modeling, and kinetic and quantum Monte Carlo (QMC).

Question 1: Approach to performing the work

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

- This project provides a very wide variety of basic science services to the recently established HyMARC. These include theory and simulation, synthesis, and in situ simulation (with many subcategories). Most of the H-storage materials were at least experimentally studied in the past, and the idea is to provide much-needed fundamental understanding of these materials, as well as establish procedures for future materials development. As such, this effort is very important to the overall U.S. Department of Energy (DOE) Hydrogen Storage Materials effort.
- The assortment of theory, synthesis, and characterization capabilities that are being developed at LLNL for the HyMARC center clearly have potential to be of value in the development of high-performance, high-capacity hydrogen storage materials.
- This is an excellent initiative, an impressive team with impressive resources. The project should detail how and why the materials investigated were selected for modeling.
- This task is led by Brandon Wood, who is primarily a computational scientist at LLNL. The proposed work uses QMC—extended crystal examining non-local chemical effects (with the help of supercomputers). These studies will permit benchmarking the various DFTs and new models for charge and field effects on physisorption—physics of sorption is being developed for graphene oxide as sorbent materials. The team will use the partnership with the National Renewable Energy Laboratory-led Characterization and Validation team to validate this model experimentally using a platform that can be synthesized. This will provide direction of interaction—theory leading experiment or experiment leading theory.
- The project is conducting a number of detailed computational studies. Given the breadth of the effort, it is unclear which specific questions are being answered or what a successful outcome would look like. Overall, the project more resembles a Basic Energy Sciences (BES)-type effort, rather than an Office of Energy Efficiency and Renewable Energy-themed study. Specific examples of how the computational methods will be validated were not very clear. This is especially true for the phase fraction predictions. It is not clear that transmission electron microscopy (TEM) has been done to assess morphology changes of the different phases vs. time/hydrogen content.

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.

- Excellent progress has been made in the synthesis of advanced porous carbons and in the development of advanced protocols to allow more accurate computation of hydride thermodynamic properties by DFT. The reviewer does not feel qualified to comment on the progress that has been made in the sorbent modeling studies, but the QMC computations seem to provide key insight into the development of physisorbents. However, the value of studies on Li_3N and PdH_x to the development of more promising systems is not clear, and the AIMD studies seem to be yielding highly questionable results. It is surprising that there is no awareness that similar studies of Ti-doped $NaAlH_4$ using soft x-rays reaching similar conclusions were reported in the literature many years ago.
- In the brief time the project has been in existence, several basic techniques have been explored and partially developed for widespread future use within HyMARC. It is too early to judge how this progress will affect progress toward DOE numerical goals. Certainly, such fundamental calculation experiment techniques will help the whole march toward the DOE goals. It is not completely clear why the particular materials for study were selected. Some are old and well established (e.g., PdH_x, $TiCl_3$-doped $NaAlH_4$, Li-N-H, etc.). Apparently, the idea is to use these as model materials to establish basic techniques.
- The proposers have developed a platform to examine the role of crystallinity (the Li-N-H nanoconfined system) and explain formation of Li_2NH (energy penalty too high for its formation in the nanophase), with a manuscript submitted. The proposers are now also doing this for the Mg-B-H system. The team has developed a statistical approach to defects: classes of defects in various fractions are used along with the likelihood of a reaction occurring. The example of the defect model given seems disconnected with the statement because the example examines nanometer size as a function of defect formation. It would be good to see more a detailed description of the defect model itself.
- Progress is good. Providing more details about the choice of materials would be nice.
- This is a new project; progress to date has been satisfactory. Many of the project components have kicked off.

Question 3: Collaboration and coordination with other institutions

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

- There are extensive collaborations, between not only the two main participants in this project (LLNL and Sandia National Laboratories [SNL]) but also other members of HyMARC. There are many faces new to the H-storage field.
- The team collaborates with the other HyMARC partners, particularly with SNL on ion-scattering (i.e., concentration gradients at interface). The team is developing collaborations with the Characterization and Validation team, particularly along the lines of examining borohydride chemistry with NMR.
- An extensive network of excellent collaborators has been established. The collaborations need to be better coordinated to enhance productivity and to keep these efforts focused on the attaining the overreaching, foundational understanding of hydrogen absorbing materials that is the goal of HyMARC.
- The project should improve or establish a relationship with Caltech work for graphene-related materials to optimize efforts.

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

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

- The modeling work is extremely important to HyMARC. Suitable progress on relevant systems is being made. Among other useful developments, the proposers are developing a part of the library system that will

include a library of nucleation barriers in the various hydride systems. If developed, this will be extremely useful to the field.
- The effort to develop hydrogen storage materials that meet DOE targets has long been in need of improved fundamental understanding of promising new systems. The capabilities being developed by LLNL have potential to provide the requisite insights into these systems.
- The project is highly relevant and could have an impact beyond hydrogen storage research and development.
- This project will not immediately address numerical Multi-Year Research, Development, and Demonstration Plan storage targets, but rather support techniques and basic science understanding for future materials development. In that sense, it is directly focused on the Hydrogen and Fuel Cells Program "chemisorption and physisorption understanding" goal and objective.
- The project may lead to improved understanding of some hydrogen storage materials. However, it is unclear whether this knowledge will be of much value in the development of improved storage materials. In other words, it is not obvious that this team is "asking the right questions."

Question 5: Proposed future work

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

- The project should emphasize new materials studies in the next presentation and justify the choices. The reviewer fully supports the choice of examining well-understood materials at this stage for model validation.
- One of the most important tasks identified in the future work is to develop an automated molecular dynamics set-up code (to speed up handling of projects that are coming online to the HyMARC computational team).
- The list of future work (slides 19–20) seems reasonable, but it is not clear why these particular tasks are the most important.
- The results of the preliminary AIMD studies should be critically evaluated before the project continues to build on what seems to be a shaky foundation.

Project strengths:

- This is an ambitious project that aims to address several critical issues in modeling and validating the properties of sorbents for hydrogen storage. This is an excellent team with excellent resources.
- The project provides much-needed basic science and experimental procedures for the general understanding of hydrogen storage materials: theory, specialized synthesis, and in situ measurement. New scientists are being added to the H-storage field.
- There are many unique aspects of the modeling proposed. The defect model is one that will be extremely useful once developed.
- (1) The efforts for the synthesis of the advanced porous carbons and computation of hydride thermodynamic properties by DFT and (2) the QMC calculations on sorbent charge effects seem to be the strengths of LLNL's effort within HyMARC.

Project weaknesses:

- There are no major weaknesses. Justification of the choice of simulation tools and modeling approaches would have been appreciated.
- The proposers must develop and define a well-communicated platform for these "theory-leading-experiment or experiment-leading-theory" interactions.
- It is difficult to understand why the specific materials and techniques are the most important to study at this time.
- The AIMD studies are giving questionable results. Soft x-ray studies have not provided any new insights.

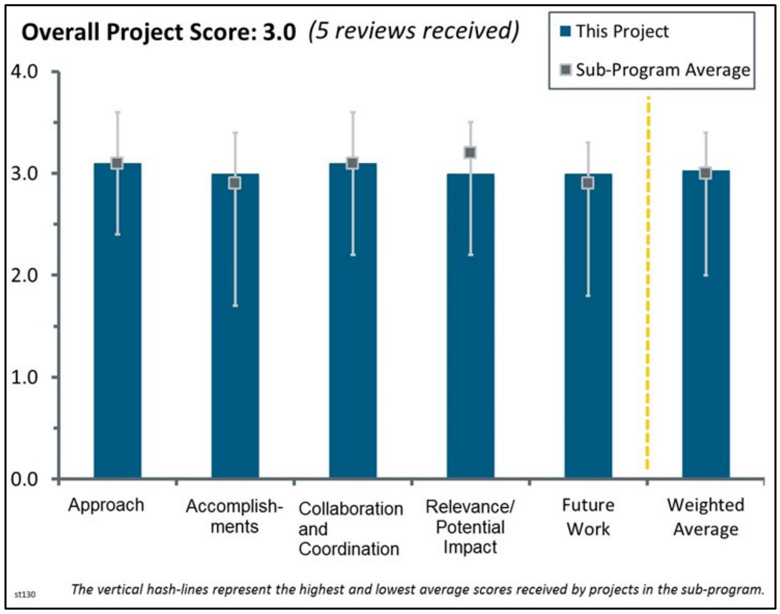
Recommendations for additions/deletions to project scope:

- Some level of work is recommended on comparing various levels of complexity of interaction potentials and how well they perform to predict high-density uptake. It was not clear whether very detailed interaction potentials are really needed for adsorption uptake calculation at high pressure/low temperature, especially with high throughput. The project should use a semi-classical Feynman-corrected potential to perform QMC calculations; it is not clear whether a full-path integral approach is needed, and under which circumstances. A "best practices" document for simulations would be a nice outcome of this project.
- The explanation of HyMARC must be restated clearly for the hydrogen storage community to fully understand its role in developing testing and validation platforms (i.e., developing the toolset to improve materials discovery). Since some materials systems must be selected and used for developing test and validation platforms, it is recommended that the team identify the test/validation platform demonstrated by each material system selected for future review cycles. No system should be selected without clearly defining its usefulness in the testing schema.

Project #ST-130: HyMARC: Lawrence Berkeley National Laboratory Effort

Jeffrey Urban; Lawrence Berkeley National Laboratory

Brief Summary of Project:



The Hydrogen Materials–Advanced Research Consortium (HyMARC) is providing community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials. Lawrence Berkeley National Laboratory (LBNL) will (1) focus on light materials and synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements; (2) design interfaces with chemical specificity for control of hydrogen storage/sorption and selective transport; (3) explore storage concepts; (4) develop in situ/operando soft x-ray characterization capabilities in combination with first-principles simulations to extract details of functional materials and interfaces; and (5) refine chemical synthesis strategies based on atomic-/molecular-scale insight from characterization/theory.

Question 1: Approach to performing the work

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

- This work emphasizes interconnection between theory, synthesis, and in situ characterization within the LBNL efforts. The strengths include the primary focus on computation, spectroscopy, and databases. All of these are important and noteworthy efforts individually, but combined, these efforts are poised to have an impact on storage systems. The team chooses to focus on (1) nanoencapsulation (Jeff Urban) and (2) multiple characterizations at the user facility at LBNL and ion scattering.
- Like ST-129, this LBNL project provides a very wide variety of basic services and materials studies to the recently established HyMARC. These include theory and simulation, synthesis, and in situ simulation (with many subcategories). This LBNL effort concentrates on the thermodynamics and kinetics of nanoscale, lightweight materials (especially Mg), and basic scientific synthesis and characterizations of various such materials. As such, this effort is also important to the overall Hydrogen Storage program. It is based more on understanding theory, techniques, and characterization than on achieving U.S. Department of Energy numerical goals within its three-year life.
- This is an important initiative. The scope seemed to overlap the work done with the other simulation team (ST-129). It would be better to clarify or differentiate the objectives of this group and explain them within the context of the overall project.
- It is difficult to judge at this early stage and with HyMARC investigating concepts and methods that address the barriers. The project does show some integration with other efforts, although some (e.g., encapsulation) appear standalone at this stage.
- There appears to be an emphasis on encapsulation of Mg. In the presentation on HyMARC by Sandia National Laboratories (SNL), it was stated that HyMARC was not established to engage in materials development; this effort appears inconsistent with that pronouncement. The meaning of the first project objective on slide 5 related to “synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements” is unclear. It is not clear why nanoscale dimensions will help meet weight and volume requirements. The physical principle behind this focus is not clear, and it is not clear

why there is an emphasis on encapsulated Mg. At the size dimensions given in the presentation of 3.5 nm, no thermodynamic change in desorption is anticipated to take place. Given differences in the nature of faceting, surface free energy and interfacial energies between this material and one that is actually suitable from a thermodynamic standpoint, whatever information that is gleaned by looking at encapsulated Mg will likely not be readily transferable to materials of actual relevance. Given that McPhy Energy already produces a commercial system based on Mg with carbon additions, this particular objective should be redirected. Also, the goal of measuring kinetics of this system is not relevant given the thermodynamic barriers, and kinetics would nonetheless be expected to be better in any system in which the diffusion distances are small. As was pointed out by one of the reviewers, hydrogen uptake in Mg has been studied extensively for the past 40 years. The encapsulation effort described here is of questionable relevance to this program. The goal of the zeolite and mesoporous SiO_2 system is also unclear. One generally knows that localized charge effects will influence adsorption. It is not clear whether the work on oxides led to schemes that are relevant to developing a material with an already known strategy to improve the adsorption process. Oxides are relatively heavy, and given the ionic or covalent nature of bonding in these materials, if the goals of this effort are met, it is not clear what strategy is in place to apply this to a material system of relevance. Finally, the goal of the computational exploration of metal–organic framework (MOF) isotherms is unclear. It is not clear what computational approaches are to be used, e.g., density functional theory or path integral methods, or why this computational effort is directed in a way that has not already been pursued by the group at Northwestern.

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.

- There are several strengths. The team has worked on solid–solid interfaces, functionalizing interfaces to promote desorption or use interfaces as barriers or membranes to prevent interaction with environment. The team is working to develop a soft x-ray hydrogen storage user community to develop from this effort at the Advanced Light Source. The x-ray absorption spectroscopy being done examines sample preparation for new materials at the beamline. These techniques will also be developed for transfer of samples for ptychography and other measurements. The team has already located discrepancies for known materials and made efforts to reconcile theory versus experiment. The weaknesses are that the scanning tunneling microscopy (STM) is only 20% complete, and no explanation is given for why this number is so low.
- In the brief time the project has been in existence, considerable work has been done according to the work plan and substantial data developed for widespread future use within HyMARC. A significant fraction of the effort has concentrated on encapsulated nano-Mg (Tasks 1, 3, and 5). Given the largely unsuccessful efforts to change the thermodynamics of Mg over several decades (crystalline, nanocrystalline amorphous, and catalyzed), the present results are not convincing that this effort is going to make much practical advancement toward DOE goals for light vehicles.
- There have been some interesting results, although performance is short of DOE metrics (rates for Mg, capacity for sorbents), with no clear strategy outlined for discovery of what factors are critical for the storage community to make progress. It is difficult to assess at this early stage.
- It is too early to judge. The progress is satisfactory at this stage (six months).
- Slide 10 shows no temperature data. The kinetics of uptake are relatively slow under whatever conditions the figure in the upper right is meant to describe. The achievement lists graphene oxide and reduced graphene oxide (rGO). It is not clear which it is. It is not clear whether enough is known about the structure of either to match to the Task 1 milestone to computational studies. While some differences in activation energies were presented, no desorption data were presented at 3.5 nm dimensions, and the thermodynamics of Mg desorption do not seem to be altered, as noted by prior work in this area that spans back 40 years. Slide 12 shows results from the graphene nanoribbon (GNR) functionalization. Not much difference is seen as a result of this functionalization. There is a depiction of the atom placement and of the repeat structure, but it is not clear how these were determined. Again, for this system, if the desorption thermodynamics have not been altered from their typical 76 kJ/mol value, it is not clear what relevance this correlation has. There was a suggestion that 95% of the density of bulk Mg uptake was achievable and that the encapsulation did not contribute substantially to loss of volumetric density. At the same time, it was suggested that the Mg particles made here were monodisperse at 3.5 nm. If these particles are spheroids, a

perfect packing density of material closer to 74% would have been expected. Slide 14 shows isotherms from materials that have presumably been modified. The assertion on the slide that a positive slope at low pressure may show an increased capacity can be extracted from the surface area data and will not go beyond one weight percent excess for these materials. What appear to be more gradual, low-pressure slopes for MCF17 and Al-MCF indicate that the Henry's law value for these materials is in fact small and the results of the modification have done nothing to improve the adsorption enthalpy over that of ZSM-5. The literature is full of data on absorption by materials of this type, and the investigators should see what has been done previously.

Question 3: Collaboration and coordination with other institutions

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

- There are excellent collaborations between LBNL and many members of HyMARC and a few external organizations. New scientists have been added to hydrogen storage research and development.
- Project results presented appear largely self-contained so far. Evidence of interaction with external partners (e.g., South Africa) appears stronger. This should improve as x-ray absorption near edge structure (XANES) modeling capabilities extend across HyMARC and hydrogen uptake measurements with SNL continue or expand.
- The strengths are that the team has developed collaboration with the University of Cape Town, South Africa. The team will use existing collaborations with the Long group and with the Energy Frontier Research Center "on campus" to extend this work. The weakness is that it remains unclear how the team will interact with the Characterization and Validation team partners.
- It is difficult to judge at this stage; the project seemed to be well coordinated, though.
- The emphasis with other institute collaboration appears to be related to the nanoribbon work. This is of limited value in connection with an effort using Mg. Randy Snurr at Northwestern has already done an extensive computational screening of MOFs. It is not clear what is to be gained through this collaboration.

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

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

- This project is focused on advanced theory, synthesis, measurement techniques, and advanced science, and it is well oriented toward those aspects of the DOE Hydrogen and Fuel Cells Program (the Program) goals and objectives.
- HyMARC has been designed to advance progress in the Program by understanding phenomena inhibiting development of materials, meeting targets, and by developing tools and methods to investigate new candidate materials. The project supports these goals, and future progress may provide impact toward this.
- Developments of nanoconfined high systems have been made, which is a strength. Following the Nature Communications work by Cho, Ruminski, Aloni, Liu, and Guo for graphene oxides, which was done in nanoconfinement to 3.5 nm in size and was looking for pressure effects at 200°C to 300°C, Mg-GNR is the next system that may be used to effectively encapsulate. Another unique idea is the field approach, i.e., using silica support that has local charge with Lewis acid and Bronsted acid sites. This is unique and broadly applicable to many materials. The question about scale of the investigated systems remains a weakness. It is not clear whether these materials are so esoteric that they will not drive the development goal. The leadership should identify broadly applicable aspects of the "boutique" materials for furthering the goal of HyMARC.
- It would be interesting to address the justification behind the choice of materials (model validation, relevance to automotive applications, etc.) during the presentation.
- It is not clear how the studies performed here will lead to the design or improvement of materials that have not already been established empirically or theoretically. Some of the analytical tools are potentially useful if they, in fact, offer insight on hydrogenated materials/surfaces.

Question 5: Proposed future work

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

- The project should continue as planned. The proposed future work should help clear up some old mysteries and provide some more firm experimental techniques for use in HyMARC and other DOE projects.
- Some of the proposed work is a generic continuation of current studies. The nanoscale $Mg(BH_4)_2$ proposed work may integrate well with other projects (ST-129); interpretation of metal hydride spectroscopy and interfacial electronics may provide valuable understanding of reaction mechanisms and kinetics to guide progress in materials design.
- A series of proposed experiments to further validate and test systems is suggested. Although computational work is suggested for XANES data validation, it would be useful to see computational work described for other areas of future study.
- The work described on Mg will be of no value to the Program. The work on borohydrides is of interest. The effort on plasmonic studies is unclear. It is not clear what energy inputs are required to initiate plasmons and why this is of interest.

Project strengths:

- The project will improve our fundamental knowledge of a variety of solid-state hydrogen storage materials and will help add new scientists to the hydrogen storage field.
- The rigorous approach to model validation is a project strength.
- Unique experimental approaches are being taken. The materials systems under investigation are relevant.
- The project has some interesting materials properties and has made progress in understanding of x-ray spectroscopy.

Project weaknesses:

- There is possible overlap with ST-129 on C-coating of hydrogen storage materials.
- The team has yet to define specifics with respect to broader goals—such as how it will interact with the Characterization and Validation team.
- It would be important to further clarify the scope of the project within the context of the overall initiative. The project should justify more clearly the selection of materials.
- The project appears too defocused for a relatively small project and has too many thrusts. Much of it seems directed at materials development (e.g., encapsulated materials and aluminosilicates) with less emphasis on an understanding that will provide a foundation for new materials across the Program. The transition metal doping of Mg could provide new knowledge, but the encapsulation with rGO confounds interpretation, and future plans appear to have shifted to alanates. It appears that HyMARC could be better focused and coordinated to address materials bottlenecks in a new way. The somewhat scattered nature of this project is part of that impression.

Recommendations for additions/deletions to project scope:

- The explanation of HyMARC must be restated clearly for the hydrogen storage community to fully understand its role in developing testing and validation platforms (i.e., developing the toolset to improve materials discovery). Because some materials systems must be selected and used for developing test and validation platforms, the team should identify the test/validation platform demonstrated by each material system selected for future review cycles. No system should be selected without clearly defining its usefulness in the testing schema.
- The project should remove the metal hydride encapsulation effort and remove the Lewis acid effort on silica templates. While plasmonics are trendy, it is not clear why their application is relevant to the Program, and they should be deleted.
- There does not appear to be a need to investigate the aluminosilicate materials proposed here. The control and understanding of Bronsted versus Lewis sites appear poorly conceived, and the nature of the sites has apparently not been investigated. The performance of the one material examined is significantly inferior to

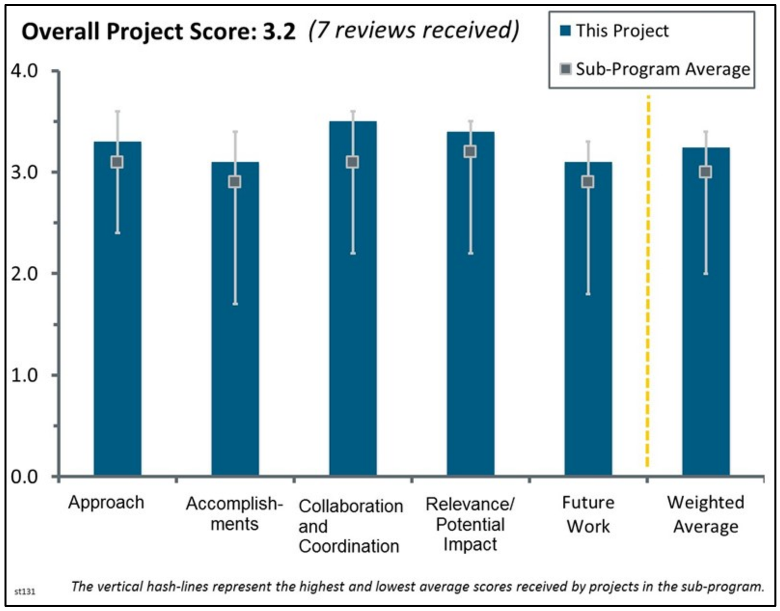
existing sorbents, and the work does not integrate with the rest of the project. It appears that this could profitably be dropped to make more rapid progress in other areas.

Project #ST-131: Hydrogen Storage Characterization and Optimization Research Efforts

Thomas Gennett; National Renewable Energy Laboratory

Brief Summary of Project:

This project represents a collaboration between national laboratories to investigate the properties of promising new hydrogen storage materials. The National Renewable Energy Laboratory (NREL) leads the collaboration, which includes Lawrence Berkeley National Laboratory (LBNL), Pacific Northwest National Laboratory (PNNL), and the National Institute of Standards and Technology (NIST). The objectives are to (1) develop new characterization capabilities such as nuclear magnetic resonance (NMR) spectroscopy, diffuse reflectance Fourier-transformed infrared spectroscopy (DRIFTS), calorimetry, diffraction, and scattering; and (2) validate performance claims and theories critical to the design of new hydrogen storage materials.



Question 1: Approach to performing the work

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

- This project combines the unique diagnostic capabilities primarily at NREL, LBNL, PNNL, and NIST to extend and complement assessments of candidate hydrogen storage materials with the Hydrogen Materials–Advanced Research Consortium (HyMARC) and independent Fuel Cell Technologies Office (FCTO) projects. Providing this resource for comparative assessments of experimental measurements of the critical gravimetric and volumetric capacities of candidate hydrogen storage materials is imperative if progress in future discovery projects is to be successful. Widespread and timely dissemination of this work is needed, along with explicit documentation of all sources of errors and development of practical protocols.
- The approach focuses on validation and characterization of hydrogen storage properties in sorbent materials. An extensive array of advanced diagnostic tools and computational capabilities is being employed by the NREL-led team to address critical issues and major barriers. The approach is well formulated, and it provides a solid foundation for achieving rapid progress that should affect and enhance our understanding of physiochemical properties and reaction mechanisms in hydrogen storage materials. A qualified team capable of validating performance claims and theories serves an important role in the overall U.S. Department of Energy (DOE) Hydrogen Storage effort.
- This project is very relevant to DOE barriers, especially relative to characterization techniques and to validating claims, concepts, and theories of hydrogen storage materials developed by others. It is primarily a four-party effort, with an NREL lead coupled with LBNL, PNNL, and NIST. As such, this helps to avoid duplication with other DOE efforts, especially those active within HyMARC. Validations of problematic outside claims, including those of other DOE contractors, are very important. The overall approach is sound. International standardization of pressure-composition isotherm (PCT) testing is very important; this project is the main worldwide effort in this area. Development of thermal conductivity measurement techniques is valuable to all DOE projects involving the engineering applications of solid-state H-storage materials.

- NREL has developed a number of tools for the measurement and analysis of adsorbent materials necessary for the Hydrogen Storage program. The work on validation that NREL performs for other laboratories is an important service, and the variable temperature work will be of value, if adsorbents with reasonably constant isosteric heats are ever developed.
- This is a solid approach to developing more in-depth techniques for characterizing adsorbed hydrogen, including a broader temperature range for PCT measurements, DRIFTS, and calorimetry measurements; incorporating neutron scattering and diffraction techniques; and overall, providing a capability for the validation and verification of hydrogen storage materials and/or concepts. The effort also supports a very good NMR effort at PNNL, which can be valuable in helping to characterize complex metal hydride systems, but this effort seems to lie outside of the core interests of the overall collaboration, which is adsorbed hydrogen. The stated objective is to provide validation. The group should be judicious in selection of the materials chosen to validate concepts to ensure (1) that they are making the right model material choice but (2) that there is appropriate involvement of appropriate materials synthesis experts to provide said material. The catecholates as probes of metal binding energetics is perhaps defensible; the extension to placing metal catecholates on nanotubes was not well supported and seemed to stretch the validation of the concept theme.
- Development of core capabilities would be of more value if there were more users in need of these capabilities. Given the rather small size of the DOE storage portfolio, there does not seem to be a critical need for these facilities.
- The approach of the group seems rather random and focused on the existing capabilities or interest of the partners rather than identifying the characterization method gaps and high-priority needs of the researchers to accelerate material discovery.

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

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

- To date, the effort has successfully collaborated in reproducing LANL capabilities at NREL in variable temperature and variable pressure calorimetry, and is developing a low-temperature/high-pressure PCT instrument that will be valuable to the community. The effort has been valuable in bringing a vastly better understanding of how to accurately and precisely measure hydrogen sorption, and how to report the results. This is not a trivial task, but it is one that the project has done exceedingly well and that helps improve the science being done in the area of sorbents. The round robin on volumetric capacity using standard materials that they have run has turned out to be highly enlightening and valuable to the sorption community, and brought greater confidence to DOE and DOE's ability to assess progress and claims among various projects.
- The thermal conductivity work is continuing and will provide data of value to modeling efforts, especially with regard to electronically insulating materials. The volumetric data of slide 11 is particularly informative and is illustrative of the range of data that should be reported by all studies involved with work of this type. The round robin may be of some use in informing particular laboratories of the reliability of their measurements, if the participating laboratories take the time and effort to evaluate their data. The Ca oxalate data are particularly intriguing. It is hoped that the observed effects and explanations are published soon.
- There has been much useful progress in the first nine months of this project. This is expected, given the large number of researchers involved. This work has covered a wide variety of materials and techniques, including development and use of characterization hardware (PCT and thermal conductivity). All of the progress is clearly useful to other DOE activities. Management of the round-robin testing effort has been excellent.
- This is a new project; progress has been satisfactory during the first few months of operation.
- The accomplishments of the project are good for just having started many of the initiatives. The inconsistent effects of the metal on desorption temperature should be further studied. It would be helpful to identify the current state of characterization and the progress of the team to improve or enhance these methods.

- The project is off to a strong start. Initial results, especially in the areas of characterization and validation, are very encouraging. The results on the effect of metal cations on desorption temperature in oxocarbons are intriguing (albeit puzzling). Although results obtained from that work might motivate additional study, the low gravimetric capacity in these systems essentially eliminates them as relevant candidates for further work (unless a dramatic new approach to enhance the capacity is forthcoming). If those materials are indeed eliminated, a fallback position involving other systems will need to be developed by the team and communicated to the FCTO. Good preliminary results have been obtained on single-walled carbon nanotube (SWCNT) sorbents and other ultra-microporous materials. However, the same concern about their relevance to supporting DOE goals applies. Close collaboration with NIST is facilitating solid progress.
- Since this team started most of their collaborative tasks during fiscal year 2016, the progress on joint work involving complementary techniques is really quite good, although establishing productive interactions with the HyMARC partners should receive some additional attention. Granted, it is not always straightforward to define common goals and plans. NREL has done well with both the thermal conductivity apparatus development and updating PCT methodology for addressing the challenges of reliably measuring the volumetric capacities. The improvement to the PCT systems for more direct determination of heat of reaction from variable temperature measurements should be an important new resource. It is less clear how much value there can be gained from the physisorption studies reported on slides 14–16. With gravimetric uptakes of ~1 wt.% or lower, even if desorption temperatures are higher; these materials seem to be very poor practical candidates to achieve the DOE hydrogen storage targets.

Question 3: Collaboration and coordination with other institutions

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

- There are numerous outstanding collaborations among the four partners, HyMARC, and other outside researchers and organizations.
- Excellent collaboration was exhibited in the round-robin sample exchange for sorbents.
- Strong collaborations are evident.
- The potential for very productive joint studies is high from these partners. A number of mutually beneficial joint efforts are either starting or currently underway between NREL and its partners on some specific materials such as the metal–organic frameworks (MOFs). Collaboration with the current HyMARC team appears a little slower but is improving.
- The project involves a high level of collaboration among the partners by the nature of the team. The internal collaboration effort description was helpful in identifying the interaction of the team. It was also useful to have the information about the collaborations with HyMARC.
- Extensive collaborations among researchers in this project and external investigators are evident. The project is well managed, and the activities appear to be well coordinated. This effort directly complements work on the companion HyMARC project. However, at this stage in both projects, the collaboration and cooperation by researchers in the two projects appears limited. It will be important to improve/enhance collaboration between the two projects in the near future.
- Collaborations with laboratories with differing expertise are ongoing.

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

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

- Bringing accurate and reproducible sorption measurement protocols to the community is invaluable, as it inspires greater confidence in interpreting reported, well-performed measurements.
- While the combined NREL team and HyMARC efforts are still evolving, the reviewer is very optimistic that significant characterization and validation results will be achieved through diverse and rigorous utilizations of in situ measurements with neutron scattering, NMR, and DRIFTS studies that complement enhanced PCT determinations of hydrogen storage capacities. Such information should provide critical

insights into the various theoretical efforts on identifying and verifying reliable mechanisms for promising hydrogen storage materials.
- This project is an important component of the DOE Hydrogen and Fuel Cells Program (the Program) portfolio. It directly complements and supports the companion HyMARC effort, and it provides a valuable resource to DOE for expert validation of performance claims and theories relevant to emerging hydrogen storage materials.
- There is no question that the research and development activities are aligned well with the Program and DOE RD&D objectives and have the clear potential to advance progress.
- This project has high relevance since the team can provide valuable tools for researchers (variable-temperature PCT, high-pressure thermal conductivity, etc.) to evaluate materials. The linkage between the characterization techniques and the targeted attributes for improvement could be highlighted to further improve the relevance of certain work streams within the effort.
- Relevance will be driven by how often the new measurement capabilities are used. At this stage, the user base is small.

Question 5: Proposed future work

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

- The NREL-led round-robin activity on determination of volumetric capacity for a standard adsorbent would be a very valuable contribution, as the reproducibility of published values is much too often contradictory and/or misleading. Combining powerful neutron and NMR assessments to probe the actual reactive species within high-potential borohydride phases and MOFs is very worthwhile. Assessing the potential for the in situ thermal conductivity and DRIFTS techniques is appealing. More emphasis on preparing to evaluate new candidate materials from HyMARC and future independent funding opportunity announcement (FOA) projects should be made with less effort devoted to those much less promising systems with hydrogen capacities <2wt.%, even though they could serve as models.
- The plan for the future is quite reasonable. It is a little hard to be sure all of the activities do not overlap with other DOE-funded projects, past and present. The close coordination among the four partners, HyMARC, and other collaborators seem to minimize the chances for that.
- Proposed future work follows straightforwardly from initial efforts. A complete and compelling description is provided. A candid evaluation of the metal-oxocarbon and SWCNT work is needed. Given the limited time and resources that are available, focusing on low capacity systems may be ill-advised.
- The focus on the metal catecholate work seems to be shifting from validation to much more detailed characterization than was justified.
- The proposed future work appears to be focused on material development rather than the characterization techniques. It would be beneficial to highlight the linkage between the future work in the area of material development with the advancements in characterization.
- Most of the future work that does not rely on outside participation is logical.

Project strengths:

- A well-qualified team with extensive experience in all areas relevant to the project objectives is conducting research on this project. The project is well managed, and good collaboration among participants is evident. The project fills an important need for DOE, especially with regard to unambiguous validation and testing of performance theories and claims in emerging hydrogen storage materials. The access to advanced characterization tools developed on this project will be of great benefit to the hydrogen storage community.
- Excellent sorption characterization capability is being augmented with new capabilities for characterization of sorbed hydrogen. The project has done an excellent job of bringing a greater understanding of sorption characterization to the materials synthesis community, which will improve the quality of data being reported.
- There are strong characterization and materials property validation efforts. New people are involved and working with more established materials researchers. The work on sorbents is important.
- NREL expertise in characterizing and validating the hydrogen storage capacities for diverse classes of materials is a valuable attribute, and enhancing the ability to perform measurements of isotherms at

multiple temperatures would be a great benefit for obtaining heats of reactions. It would be especially useful if NMR, neutron scattering, and infrared/Raman spectroscopies could substantiate whether conflicting empirical or model interpretations could be either verified or dismissed for these macroscopic properties.
- The strength of the project is the highly collaborative effort with the key researchers in the field of characterizing materials for hydrogen storage. The scope of the project is important to have the necessary toolset to understand the materials characterization in order to optimize parameters.

Project weaknesses:

- There are not really any weaknesses.
- A careful consideration of research directions relative to the ultra-microporous materials is imperative. The pathways that have been selected thus far in the NREL project (e.g., oxocarbons and SWCNTs) may have serious limitations that might require a mid-course correction. A detailed evaluation needs to be done, and alternative plans (if needed) should be formulated.
- The weakness of the project is the unclear division and direction between a focus on characterization techniques and materials development. The prioritization of the effort should be coordinated based on the necessity, rather than the interest of the partners.
- The major concern with NREL efforts is their continuing focus on low-potential candidates for adsorption since similar work could be done on more promising MOFs, etc.

Recommendations for additions/deletions to project scope:

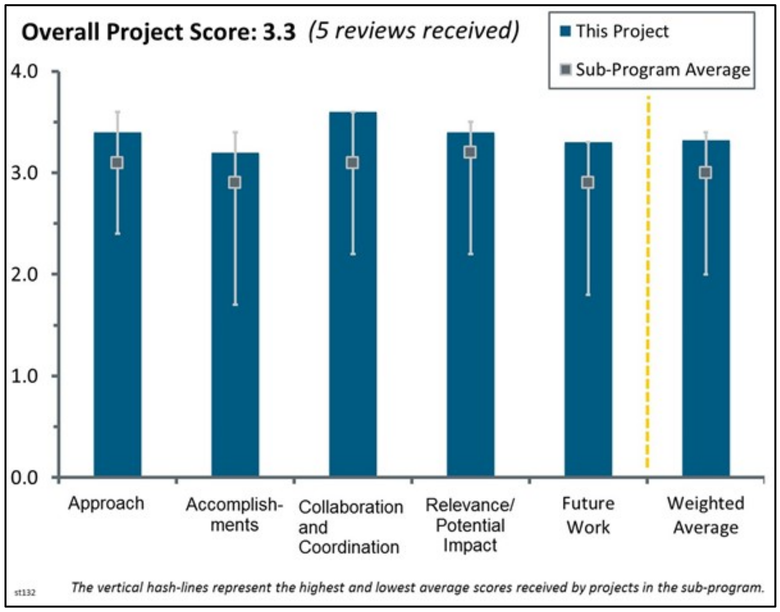
- Since the extent of characterization and validation requests from the HyMARC program and new FOA projects remains to be seen, it would be premature to make any significant changes in scope at this time. However, NREL and its partners should be preparing detailed specification and protocol documentation that facilitates submission and handling of samples suitable for characterization without compromising integrity of the materials during processing or the experiments. A review panel (perhaps with outside advisors) should assess and prioritize candidates to select those most likely to benefit from the use of the available instrumentation. Continuing to evaluate either oxy-carbon or catechol-based materials is not recommended unless they have the potential for storing more than ~5 wt.% hydrogen, as there are several more promising candidates worthy of such detailed assessments.
- Closer collaboration with HyMARC investigators is strongly encouraged. Although increased inter-project cooperation is part of the project plan articulated by the NREL team, each group appears to be operating primarily independently. In order to achieve significant impact in the “rational design of new materials,” the NREL team and HyMARC investigators should be engaged in a more direct way. This can be a potent collaboration that directly supports the overall Hydrogen Storage program goals.
- The project should be judicious in choosing areas that can be adequately justified in terms of either providing greater understanding of a concept or providing validation of a material. Other efforts in materials synthesis may be distractions from the main stated objective.
- The recommendation for the project scope is to evaluate the current state-of-the-art characterization methods and determine the gaps or areas of improvement to make the most significant impact in advancing materials discovery for hydrogen storage.

Project #ST-132: Hydrogen Storage Characterization Research Efforts

Tom Autrey; Pacific Northwest National Laboratory

Brief Summary of Project:

This project is part of a collaboration between national laboratories to develop new characterization capabilities to investigate the properties of promising new hydrogen storage materials. Pacific Northwest National Laboratory (PNNL) will focus on nuclear magnetic resonance (NMR) spectroscopy and calorimetry to complement parallel efforts at other national laboratories. The project will also work toward validating claims and theories critical to the design of new hydrogen storage materials that show promise.



Question 1: Approach to performing the work

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

- In this new fiscal year 2016 project, PNNL will primarily perform specialized high-resolution NMR experiments in order to identify reaction pathways for hydrogen absorption, adsorption, and desorption processes. In contrast to most prior NMR assessments, the PNNL measurements will be conducted largely in situ over large ranges of both temperatures and pressures that correspond much more closely to operating conditions in hydrogen storage applications. This information can potentially provide very detailed insights into the atomic-scale behavior in practical environments and also test whether theoretical mechanisms are valid. In some cases, the NMR studies will be in conjunction with reaction calorimetry and modeling efforts at PNNL, as well as collaborative neutron scattering, infrared (IR) spectroscopy, and other techniques with the National Renewable Energy Laboratory (NREL)-led Characterization and Validation team and the Hydrogen Materials–Advanced Research Consortium (HyMARC). Eventually, promising materials from the new funding opportunity announcement (FOA) project would be provided for the advanced in situ NMR characterizations.
- The approach has a rational design—understanding chemistry to characterization—and the team will interact with groups developing new materials using its tools. The work brings together complementary research tools, including NMR and calorimetry, to complement NREL, neutron scattering at the National Institute of Standards and Technology (NIST), and studies done at Lawrence Berkeley National Laboratory (LBNL). The current focus is on validation of the cycles between BH_4 and $B_{10}H_{10}$ on a Mg system. Additional focus is being placed on the development of additives using rational design.
- This project focuses on a number of U.S. Department of Energy (DOE) barriers, in particular N (Understanding of Hydrogen Physi-and Chemi-Sorption) and O (Evaluation Facilities). Characterization efforts include NMR and reaction calorimetry of both physisorption and chemisorption materials. This project aims at developing the fundamental understandings of hydrogen storage materials to help validate others’ claims and to aid future DOE efforts toward practical solid- and liquid-state hydrogen storage materials. The scope of the work is nicely compartmentalized to complement the related objectives of the partners NREL, NIST, and LBNL. The approach is very reasonable.
- PNNL’s approach to working within the Characterization and Validation team and collaborating with HyMARC is to bring state-of-the-art NMR capabilities to bear on materials of interest ranging from sorbents to complex hydrides to chemical hydrogen storage materials.

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 science is very strong. Because the NMR Pake pattern width depends on hydrogen dynamics and the work will collaborate with inelastic neutron scattering (INS), it provides a broader view of hydrogen dynamics than would be possible without this collaborative effort.
- At this point, the project is demonstrating the viability of the approach of using NMR techniques to gain information about reaction enthalpies of sorbents, hydrides, and chemical storage materials. Additionally, the researchers have demonstrated that low-temperature solid-state NMR may be used to help characterize hydrogen on metals bound to sorbents and have shown that these data are highly complementary to INS. It will be interesting to see how much information can be extracted from the NMR data at variable low temperatures. Using solution NMR and reaction calorimetry in a commercial calorimeter to characterize hydrogenation products or heats of hydrogenation/dehydrogenation is too routine to be considered novel or innovative, and researchers who would be interested in these sorts of materials systems would very likely have such capability. On the other hand, the high-pressure in situ solution and solid-state/MAS NMR capability using PEEK sample tubes is very nice, and that would seem to be readily transferable to those interested in adapting similar high-pressure NMR sample containers for the solid or solution state to their own facilities. So that is a valuable contribution to the field and will likely find a lot of use by those interested in the Mg-B materials system. The hypothesized reaction network in the Mg-B hydrogenation system mapped using Wade's Rules is thought-provoking and may help to decipher the reaction network. Perhaps there will be some clues regarding kinetics barriers among one or more of those possible intermediates that may shed light on the underpinning kinetics issues of the hydrogenation/dehydrogenation of Mg borohydride.
- Much of the PNNL effort has been to adapt or develop the specialized NMR instrumentation required to permit the desired in situ studies over the extended environmental conditions. These are generally not trivial modifications and resulted in PNNL mostly performing various initial feasibility experiments. The expectations are to generate more tangible results within the next several months that will explicitly provide insights on the detailed compositions of species involved during reactions with the desired hydrogen storage conditions.
- The project is new; good progress has been made in less than one year's time.
- Good progress has been made in the first eight months of this project in areas of NMR, reaction enthalpy, surfaces, and reaction paths. There is a wide range of material-technique combinations involved in this work. The presentation does not make it completely clear why these particular combinations were chosen from among other possibilities.

Question 3: Collaboration and coordination with other institutions

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

- There is an outstanding list of partners, collaborators, and interactions with HyMARC (slide 2). It is very encouraging to see some international collaboration with International Energy Agency–Hydrogen Implementing Agreement Task 32 and Japan's National Institute of Advanced Industrial Science and Technology (AIST).
- The project clearly has very good collaboration within PNNL in the NMR area and is bringing that capability to HyMARC and the Characterization and Validation team.
- PNNL has already initiated several collaborations to utilize NMR to probe details of bonding and reactions of hydrogen with adsorption media and the magnesium borohydride–boranes–borides. A caveat is to ensure that sample processing and handling do not compromise the integrity of the often highly reactive and air-sensitive materials. Presumably, PNNL will make the appropriate instruments available for measurements to members of the HyMARC and others.
- Strengths include that the work involves a broad network of collaborations on $Mg(BH_4)_2$ systems, including with Craig Jenson, Brandon Wood, Vitalie Stavila, Bob Bowman, and international groups. Other key and strategic collaborators include visiting professor Gary Edvenson to develop Wade's Rules to predict

structures and reaction pathways. A weakness is that the work clearly overlaps with the other Characterization and Validation team groups—but overlaps with HyMARC are not so obvious.
- Very strong collaborations are evident.

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

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

- Adding NMR signatures to the overall set of signatures in the broad family of hydrogen storage materials is highly relevant and can have an impact by providing guidance and validation to experimental and computational efforts.
- In situ NMR spectroscopy of the hydrogen isotopes as well as host elements (and catalysts in favorable circumstances) has outstanding potential for providing quantitative details on the microscopic species and competing reactions that determine both reversible and irreversible reactions of the hydrogen storage media. These studies should strongly complement other methods, including neutron scatting, vibration spectroscopies, and electronic spectroscopies to verify or defunct theoretically proposed mechanisms. Clarifying the responsible and possibly competitive processes should help establish the potential and limitation of proposed storage candidates, including the roles of additives/dopants.
- The strengths include that a unique toolset is being used (to examine relevant storage systems: $Mg(BH_4)_2$). Likewise, rational design of the selection of additives (and criteria for selection of them) is a nice feature of the project. A weakness is that little discussion has been given to systems to be studied beyond the Mg-B-H system.
- The project clearly supports and advances progress toward the DOE Hydrogen and Fuel Cells Program goals and objectives as delineated in the most recent Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan. However, it should be noted that progress within the three-year projected life of the project will be mostly understanding fundamental science and techniques rather than achieving the practical DOE targets of weight and volume.
- The project is mostly focused on addressing important phenomena involving relevant materials.

Question 5: Proposed future work

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

- The specific tasks being conducted or initiated at PNNL via NMR and other methods all have merit to either demonstrate feasibility or test proposed models and concepts. It is important that modifications can provide suitable pressure and temperature conditions to mimic those found in practical hydrogen storage applications to permit consistent comparison with empirical and theoretical reaction mechanisms.
- PNNL has a good plan to map onto the Characterization and Validation team needs and HyMARC needs and fill gaps in capability. It also brings some chemical science expertise and intuition to the overall effort.
- The addition of computational studies, particularly on the binding energy of hydrogen, is suggested. INS and QENS will be undertaken to complement the NMR studies to get more information on the important effect of hydrogen dynamics. These are a useful set of future plans.
- The proposed future work seems logical. The two go/no-go decision points (slide 29) may be difficult to achieve.

Project strengths:

- PNNL possesses numerous advanced NMR spectrometers that should be capable of greatly enhancing the sensitivity and selectivity of measurements on viable hydrogen storage media. The breadth of capabilities of these instruments should provide much greater potential to probe details of processes responsible for their behavior. Many PNNL staff members possess strong expertise in NMR and other characterization methods, and have knowledge and experience with diverse hydrogen storage materials.

- Project strengths include the strong emphasis on extending the state of the art of NMR technology for adsorbents and chemisorbents, strong national and international collaborations, and the new scientists in the hydrogen storage materials area.
- Overall, this is a very strong project. The plans for studying storage-relevant systems are broad and are poised to provide unique insights into material dynamics.
- There is an extremely strong institutional effort in state-of-the-art NMR at PNNL, and this project can provide some access to that capability.

Project weaknesses:

- Perhaps this is not a weakness, but the calorimetry and conventional solution-state NMR capabilities presented are likely available at any institution where there would be an interest in addressing hydrogen storage materials such as chemical hydrides.
- Little discussion beyond the Mg-B-H system is provided. The additives being developed (and/or the rational design approach to their development) could possibly work well for other storage systems.
- To obtain the comprehensive data necessary to derive in-depth assessments of the hydrogen storage materials, substantial time on specialized NMR systems probably will be needed. This requirement may be in conflict the with "user facility" status of many instruments that operate in PNNL's Environmental Molecular Sciences Laboratory, limiting the needed time to perform the experiments.
- There are unclear justifications for all the materials selected for study.

Recommendations for additions/deletions to project scope:

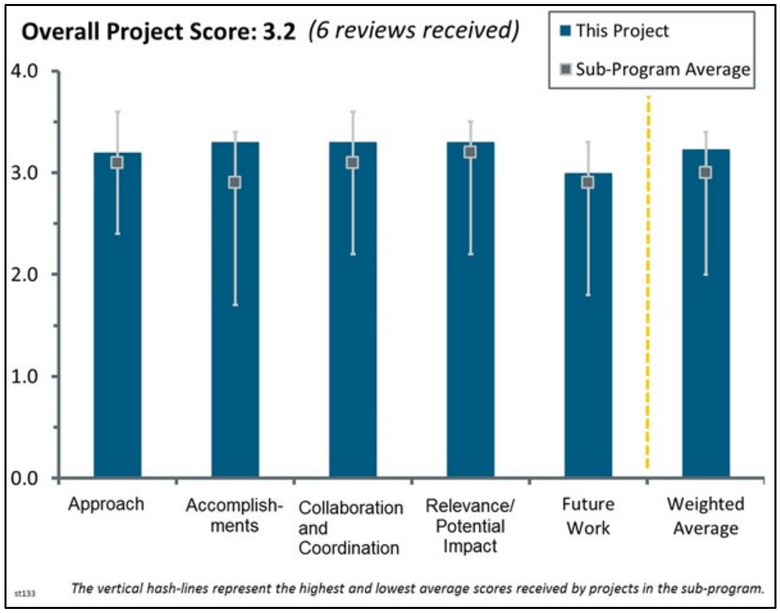
- Assuming the feasibility experiments with the adapted NMR systems are successful, at least one or more carefully integrated investigations involving the combinations of in situ characterization techniques should be conducted with PNNL partners to address issues such as whether more than two hydrogen molecules can bond to metal sites in a well-defined metal–organic framework or whether catalysts can promote kinetics and improve reversibility for a high-capacity borohydride.

Project #ST-133: Hydrogen Storage Characterization and Optimization Research Effort

Jeffrey Long; Lawrence Berkeley National Laboratory

Brief Summary of Project:

This project is part of a collaboration between national laboratories to develop new characterization capabilities to investigate the properties of promising new hydrogen storage materials. Researchers will also validate new concepts for hydrogen storage mechanisms in adsorbents and provide accurate computational modeling for hydrogen adsorbed in porous materials. Specifically, Lawrence Berkeley National Laboratory (LBNL) is developing in situ infrared (IR) spectroscopy as a tool for characterizing emerging hydrogen storage materials as well as developing metal organic framework materials that will allow for more than one hydrogen molecule per open metal site that will increase hydrogen capacities for sorbent materials.



Question 1: Approach to performing the work

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

- Leading-edge work on high-capacity hydrogen storage in metal–organic framework (MOF) sorbents is being conducted in this project. The approach is innovative and is keenly focused on long-standing barriers to achieving high-capacity storage at elevated temperatures in sorbent systems. The M_2(*m*-dobdc) and M_2(dsbdc) systems are showing great promise for high-capacity storage. The approach that has been employed to exploit the unique properties of these materials is novel and is producing useful results in a timely way.
- The approach to MOF synthesis is to focus on designing and synthesizing MOFs with strong binding sites, such as metal cations with incomplete coordination spheres. This strategy is well known to these investigators and builds on prior work over several years. A structural isomer of MOF-74 is the initial focus. Synthesis, characterization, and modeling are being carried out to determine where hydrogen binds and the nature of the interaction.
- The approach is good overall.
- The approach was focused on materials development and mechanistic validation of binding multiple hydrogen molecules per metal cation, which was important to demonstrate, but the project seemed separate from, rather than part of, the Characterization and Validation team.
- This is a relatively new project designed to bring in situ IR capabilities to hydrogen materials analysis. This effort also continues a prior effort to research coordination polymer-type materials. There were too many introductory slides. Slide 10 shows a plot for pure hydrogen that is incorrect. Hydrogen density is not linear over this range, and at 100 bar, it maxes out at 31 g/L.
- The title of this project conveys the impression that it will have a rather broad scope; however, the LBNL presentation itself indicated that the work is apparently limited to only specific transition metal-containing MOFs with the tenuous potential of bonding two or more hydrogen molecules on the metal locations. Comparisons of the specific MOFs that would nearly meet the DOE "SYSTEM" volumetric target shown on slide 8 are very misleading. For example, the principal investigator (PI) states on slides 17, 18, 21

(although he does say it is “maximum” capacity), 40, and 50 that the MOFs are close to the DOE volumetric target of 40 g H_2/L, but this will be reduced by a minimum factor of two when the storage volume is included.

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.

- Excellent progress has been made on the project during this reporting period. Important results that are greatly improving our understanding of hydrogen binding to metal-containing MOFs have been obtained. The studies of hydrogen sorption on Ni_2(*m*-dobdc) and Mn_2(dsbdc) are especially noteworthy. The first example of multiple binding of hydrogen molecules to a single metal center in a MOF (Mn_2(dsbdc)) is an important and impressive achievement. The results obtained from variable temperature/pressure in situ IR spectroscopy have highlighted the importance of that characterization technique for measurement of site-specific adsorption enthalpies. On a separate note, given the unique information that can be obtained from those measurements, it is surprising that the variable temperature/pressure in situ IR measurement capability is available only at Oberlin College and not at one of the partner institutions (e.g., NREL). The availability of the instrument at one of the project collaborators would obviate the need to develop the capability at LBNL.
- The project made excellent progress in confirming the multiple hydrogen binding to an open metal site (OMS), which was a significant step toward the viability of this mechanism, even though the results of the multiple binding did not provide advanced performance for the particular material evaluated. It appeared that some of the MOF-74 material effort with *m*-dobdc was developed previously.
- The effort to develop the DRIFTS spectrometer is on track. An instrument has been ordered following evaluation of several designs. The Ni_2(*m*-dobdc) MOF shows higher uptake at all $T < 100°C$ than compressed hydrogen up to 100 bar. Capacity of this material is 58% of the system target if a temperature swing is used. Collaboration with NREL verifies accuracy of high-P isotherms measured at LBNL. A very significant result is the demonstration that two hydrogen molecules can bind to a metal center in a MOF. The MOF used is not relevant to hydrogen storage because of gravimetric capacity limitations, but nevertheless this work gives hope that multiple hydrogen binding is at least possible. Modeling is providing binding geometries, and these were compared with neutron data obtained at NIST. It is interesting that the models over-predict the strength of the hydrogen–metal interaction (distances are shorter than observed). This is consistent with the predicted binding energy, which is much higher than the experiment. These calculations show the limitations of present theoretical methods and are pushing the investigators to make improvements to the models. Modeling does show that replacing Mn in the structure with Ca should increase the binding energy. New catecholate MOF structures look promising, although the nearly identical binding energies predicted by theory are curious and seem unlikely to be borne out in practice. Other MOFs with potential for binding more than one hydrogen per metal are being synthesized.
- This effort has just begun, so accomplishments are somewhat limited at this point. A number of the viewgraphs covered prior research efforts and were not necessary. Expanding on details of the Mn_2(dsbdc) structure would have been of more value. It appears that the structure, as an isomer of the *m*-dobdc material, has a similar loading to the *m*-dobdc material, which should not be surprising. What is curious is the low but nearly constant isosteric heat. This appears to run counter to the higher isosteric heat that was calculated as shown in slide 29. The charge transfer in this case was presumably calculated using a fragment of the actual structure. Given that two molecular hydrogens can be accommodated at the Mn site, one would expect a higher initial isosteric enthalpy of adsorption (Q_{st}) than shown in slide 26. The availability of an open metal center site for this structure appears to have made no difference to the adsorption properties over that of a dobdc structure.
- The LBNL team has an extended theoretical basis for optimizing multiple hydrogen bonding on a single metal atom in a MOF compound and has evidence for bonding two hydrogen molecules. Because a nearly constant (and low) 5.5 kJ/mol binding was shown in slide 26, schemes for significantly stronger binding will be needed to raise operating temperatures to circa 150+ K. The delays in obtaining and setting up the DRIFTS instruments are having a negative impact on the schedule.

- The demonstration of two hydrogen molecules per metal center is an important accomplishment. There is a large discrepancy between the calculations and experiments regarding the adsorption of two hydrogen per Mn in Mn_2(dsbdc). Both the energies and geometries differ significantly; the origin of this discrepancy is unclear. Several slides covering M_2(dobdc) and M_2(*m*-dobdc) were presented last year. This repetition makes it difficult to assess the quantity of new work performed.

Question 3: Collaboration and coordination with other institutions

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

- Collaborations with NREL and NIST are well established and very productive. The close link between the synthetic efforts and the theory and characterization is proving very powerful in guiding synthesis of modified structures. This is clearly the "A team."
- Extensive collaborations with partners at NREL, PNNL, and NIST are evident. Those collaborations have been important to the success achieved thus far on the project. As this project continues, it will be important to engage more actively with investigators in HyMARC who are pursuing related approaches.
- Strong collaborations exist with several partners.
- The collaboration with NIST is very good and needed for accomplishing the mechanistic validation of binding multiple hydrogen molecules per metal cation. The coordination with the other members within the Characterization and Validation team is not as defined.
- LBNL has worked very well with both NIST and Oberlin College for neutron scattering and DRIFTS characterization, respectively, of their materials. NREL appears to have provided independent confirmation on the storage capacities of the LBNL-made materials. It was not apparent from the PI's AMR presentation that roles and potential for nuclear magnetic resonance (NMR) characterization are appreciated or being included in the planning and modeling efforts. This would be an oversight.

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

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

- The assessment of predicted capacities on slide 40 appears to show marginal improvements to material capacity on the basis of crystal bulk density. Given the normal packing density of materials of this type, it is not clear that any of the newer UiO structures offer possibilities that suggest substantive improvement in volumetric density over that of MOF-5.
- The project is clearly focused on the critical limiting factor for hydrogen storage on sorbents: inadequate volumetric capacity at the temperature required (ambient, non-cryogenic) needed for practical implementation. The new IR spectroscopic tool will provide a new capability to the Hydrogen Storage program and will provide information previously unavailable except by neutron techniques. The theory effort will, for the first time, identify MOFs that have the potential to bind more than one hydrogen per OMS. OMSs are difficult to model accurately, so this effort should be able to generate binding energies for a range of structures with better accuracy than any of the previously used models. Clearly, this is critical for determining which direction to go to develop sorbents (not just MOFs; the result could be potentially relevant to doped carbons as well) that meet DOE targets. It seems likely that the project will be able to determine the limits of multiple hydrogen binding and determine whether MOFs having this property can store enough hydrogen to meet DOE targets. This project currently has the best chance of solving the sorbent storage problem of any known to this reviewer.
- If the LBNL team can prepare and demonstrate MOF compounds that allow multiple hydrogen adsorptions on most metals in the host lattice and also have binding energies factors of three to four greater than conventional physisorption materials, these materials may be viable candidates for vehicle storage. On the other hand, results obtained to date seem to indicate they are far below those required levels for both capacities and binding energies.

- The project is closely aligned with the goals and objectives of the Program. Development of high-capacity sorbent materials for hydrogen storage is an important DOE objective. This project is at the leading edge of that effort.
- This is a highly relevant project.
- The project is relevant in addressing the barriers and understanding of hydrogen storage adsorbent materials, although the support of the Characterization and Validation team is less clear within the project work.

Question 5: Proposed future work

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

- It is good to see that the LBNL team is going to concentrate on improving and adapting synthesis methods to form the MOF compounds with predicted and modeled desired properties.
- Proposed work follows logically upon the discoveries made thus far. The project definitely has its eyes on the prize, and there is little in the way of extraneous activity that is evident. The new DRIFTS instrument should be online in the near future and will be a valuable tool for other projects as well as this one.
- The proposed work is a logical and straightforward extension of the research conducted in the first year of the project. The experimental effort is well formulated and will likely result in solid progress toward project goals. However, the computational effort is not clearly described. It is not apparent whether additional theory and modeling work is needed or will be done in the next reporting period. A clear pathway to the discovery of a sorbent material that meets DOE storage goals is not readily apparent (the reviewer fully recognizes the daunting challenges that exist).
- The proposed future work is very appropriate for a materials development project, but the scope should also include support of the Characterization and Validation team.
- On slide 44 for proposed future work, the effort that is directed at dsbdc analogs is understandable for the sake of systematization, but given that these materials are isomers of dobdc structures that have limited surface area and volume to accommodate hydrogen, it is not clear that this class of structures is worth pursuing through the project. Even if higher Henry's law values are obtained, the marginal improvements to volume density suggest that other structures with OMSs or charge transfer effects that effectively alter adsorption enthalpies should be the primary goal of further effort.
- Experimental details are well described, but the computational effort is not mentioned at all.

Project strengths:

- The excellent, top-notch team integrates all needed disciplines: synthesis, characterization, and theory. The deep history working with MOFs as gas storage media is another project strength. The highest levels of theory are being brought to bear on a difficult problem. All elements of the project inform the others—theory-guiding synthesis, characterization assisting in validation, and synthesis responding to knowledge gained from the other two.
- The LBNL team has identified and prepared several MOF compounds that point to improved performance toward these materials meeting the DOE targets. Furthermore, comprehensive neutron scattering results have proven to be very valuable to validating or repudiating theoretical predictions of hydrogen adsorption mechanisms and structures. Adding new in situ NMR studies into the project should also complement and extend these assessments.
- The research and development team assembled for this project is first-rate, and the results obtained thus far on the project are most impressive. There is a clear understanding of the barriers and obstacles, and a solid, comprehensive project plan is in place to address them. Extensive internal and external collaborations are advancing the pace of progress.
- The strength of the project is the accomplishment of providing the field a first example of multiple hydrogen molecules on a single metal site. This result could provide an opportunity to increase the capacity of adsorbents significantly. Another strength of the project is the depth of the researchers on this project and their disciplined pursuit of advancing MOFs.
- The project has strong collaborations and is focused on materials of high relevance to the Hydrogen Storage program. A successful outcome will have a large impact.

Project weaknesses:

- No weaknesses were identified.
- Although notable progress has been made in this project, the fact remains that none of the materials investigated thus far meets the DOE hydrogen capacity targets. This presumably will require either an MOF having metal sites capable of binding more than two hydrogen molecules per site or a MOF with a much higher metal density. Obtaining either of these is a serious challenge, requiring an approach and material system(s) that have not yet been identified.
- In many ways, this “new” project appears to be a direct continuation of the prior LBNL work on MOFs with a down-scoped focus on multiple hydrogen molecules adsorbing on metals. The role LBNL will have to support other researchers is not apparent. It was not clarified how much time will be available for the DRIFTS instrument to perform those critical measurements on hydrogen binding energies for other research groups investigating hydrogen adsorption mechanisms.
- The weakness of the project is the focus on materials development rather than on supporting the Characterization and Validation team.
- Overall, the work presented is of very high quality. Nevertheless, this project is one of the largest in the storage portfolio, and by that metric, the quantity of research should also be high. Much of the presentation focused on older results presented at last year’s AMR. In addition, the number of new compounds explored appears to be small. Together, these observations suggest that progress is below expectations. It is recommended that the presentation more clearly call out the new work performed since the last AMR.

Recommendations for additions/deletions to project scope:

- Cycling and reversibility studies are important to fully evaluating the efficacy of these materials in a practical hydrogen sorption environment. Those studies are not currently included in the future plans. It is strongly recommended that they be incorporated as part of the ongoing work.
- There appears to be little need for continuing or extending the theoretical aspects of this project until some MOF compounds with previously predicted multiple hydrogen adsorption on single metal sites have been synthesized and are characterized with hydrogen capacity measurements at NREL along with neutron scattering, NMR, and DRIFTS evaluations. Assuming the DRIFTS instrumentation becomes operational at LBNL, it should also be used to investigate suitable samples from HyMARC and other DOE-funded researchers.
- The recommendation for this project scope is to increase the activities in conjunction with the Characterization and Validation team or allow it to be a materials development project, but it is not clear whether the project is identified as part of the team itself.