

IV.C.1a Overview of the DOE Hydrogen Sorption Center of Excellence

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Objectives

The Hydrogen Sorption Center of Excellence (HSCoE) developed high-capacity sorbent materials that operate at cryogenic to ambient temperatures and are efficiently and quickly charged in the tank with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Work was directed at overcoming barriers to DOE system goals

and identifying pathways to meet the hydrogen storage system targets. In particular, the HSCoE strove to:

- Develop high specific surface area (SSA) sorbents with optimal H binding energies with the focus to increase binding up to ~25 kJ/mol H₂ for room temperature operation. This enables:
 - High-capacity systems that operate at modest pressures (e.g., less than 100 bar) and below fuel-cell operating temperatures (<70°C).
 - Meeting both gravimetric and volumetric targets simultaneously with rapid kinetics.
 - Efficient and rapid on-board refueling with minimum energy requirements.
- Rapidly correlate capacity, structural, and energetic information to reduce time between discovery, assessment, and down-selection of materials:
 - Integrate experiment and theory seamlessly in both “feedback” (explanation) and “feed-forward” (discovery) modes.
 - Devise facile synthetic routes using low-cost approaches.
- Create a nimble and flexible, yet structured, teaming environment to accelerate discovery, evaluation, and selection of promising development directions:
 - Partners were organized in focused groups to optimize development and avoid duplication of effort, with seamless integration of experiment/theory.
 - Quantitative down-select criteria were used prior to beginning significant development and at go/no-go points.

Technical Barriers

The HSCoE developed novel high SSA sorbents to be used in hydrogen storage systems for advanced fuel cell technologies. During the past year, the HSCoE had 15 active projects at 18 institutions. HSCoE partners conducted a wide range of applied research and engineering studies on currently available sorbents and developed design principles and synthetic methods with the goal of creating next-generation materials that have the potential to meet the critical DOE hydrogen storage system targets. The technical barriers addressed by these projects from the Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration Plan included:

General:

- (A) System Weight and Volume
- (B) System Cost

- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management

Reversible On-Board:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

The HSCoE developed sorption materials for hydrogen storage systems. In general, sorbents can be used in systems to meet most of the DOE hydrogen storage targets for light-duty vehicles. Thus, the HSCoE focused efforts to address the highest-risk targets for sorbents which are primarily associated with capacity and costs, including:

- Cost: \$4/kWh net
- Specific Energy: 1.8 kWh/kg
- Energy Density: 1.3 kWh/L
- Charging/Discharging Rate: 3.3 min.

Accomplishments

The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbents. For specific details, please review their individual contributions to this report. A summary of the major accomplishments for the HSCoE overall is listed in the following.

- Designed and developed reversible sorbents via ambient temperature hydrogenation techniques that have over 4 wt% storage capacities with isosteric heats of adsorption of 10-30 kJ/mol.
 - Pioneered the development of spillover that has been validated on numerous materials and that have relatively low chemical binding of hydrogen, potentially allowing efficient reversible on-vehicle refueling. This class of materials enables hydrogen storage system designs with more than 75% of the volumetric and gravimetric capacities of the materials and substantially reduces system costs and complexity.
- Developed new materials that increased the gravimetric (~40%, e.g. from ~5 to >7 wt% at 77 K) and volumetric (~150%, e.g. from ~15 to >35 g/L at 77 K) hydrogen storage by physisorption onto high SSA sorbents by optimizing pore sizes (0.7 to 1.5 nm) to increase specific surface area and packing density.

- It may be possible to meet DOE 2015 on-vehicle refueling hydrogen storage system capacity targets with physisorption-based optimized material at cryogenic temperatures and relatively low pressures (i.e. 10 to 50 bar). The decreased pressures, compared to high pressure 350 to 700 bar storage systems, enabled by relatively inexpensive carbon-based sorbents could substantially reduce tank and balance-of-plant costs.

- Synthesized new high SSA physisorption materials with optimized uniform pore size using a variety of scalable/inexpensive processes.

- Discovered and championed an entire class of viable materials that uses lightweight (e.g. 3d metals) metal centers to enhance H₂ isosteric heats of adsorption and enable multiple H₂ binding on each metal site.
 - Initial theoretical work demonstrating multiple molecular hydrogen (H₂) binding to electronically unsaturated 3d metals (30 kJ/mol – H₂) was first performed by the HSCoE. These studies initiated hundreds of subsequent theoretical and experimental studies in the research area of strong/multiple H₂ binding. The original paper [1] has been cited nearly 200 times. This work paves the way to meet DOE's ultimate storage targets at ambient temperatures.
- Designed and developed substitutional materials with enhanced dihydrogen binding energy to increase capacities at near ambient temperatures, on a per SSA basis.
 - Substituted materials enhance hydrogen isosteric heats of adsorption (e.g. ~11 kJ/mol for B substituted carbon, compared to ~5 kJ/mol for pure carbon) sufficiently to increase capacities at near ambient (e.g. ~200 K) temperatures. Substituted materials have the potential to meet DOE's 2015 hydrogen storage system capacity targets. Increasing storage temperatures to near ambient helps decrease system costs by reducing the amount of insulation, tank, and balance of plant costs.
- Confirmed that standard physisorption-based dihydrogen adsorption scales with SSA. To date, no validated experimental evidence exists that any substantial capacity enhancements occurs due to geometric configurations.
 - At the outset of the Center, numerous publications had reported extraordinary results for high SSA materials where the enhanced capacities were potentially a result of novel geometries or structures within the material. In general, heats of adsorption can be increased

with multiple wall interactions in very small pores, but this ultimately reduces capacities. The Center did not validate any single element material or any materials with unexceptional electronic states that have substantially higher hydrogen storage capacities beyond what is expected based on the SSA and specific storage conditions.

- Developed unique measurement capabilities to accurately and reliably characterize hydrogen storage properties.
 - Neutron scattering.
 - High-pressure H₂ nuclear magnetic resonance that performs measurements from 77 K to ambient.
 - Hydrogen storage properties with small laboratory-scale (1-100 mg) samples:
 - Enables high throughput and rapid screening analysis:
 - Accurate hydrogen storage property measurements a major problem in the community for decades.
 - Partly due to only having small quantities of “laboratory-scale materials” to characterize.
 - Developed protocols and measurements capable of accurate results from small amounts of sample:
 - Substantially enhanced throughput by eliminating need to develop larger scale synthetic methods or repeating synthesis processes numerous times to make enough material.



Introduction

To realize the full energy efficiency, energy savings, and environmental improvements that fuel cells can provide, significant improvements over currently available high pressure-based gas storage technologies are required. The storage targets presented in DOE's FCT Program Multi-year Research, Development and Demonstration Plan state the critical needs and goals. To improve the mass, volume, cost, safety, and efficiency requirements for vehicular or early market storage systems, DOE is investigating solid-state storage options such as metal hydrides, chemical hydrides, and sorbents. Nanostructured high surface area materials containing carbon, metals, oxygen, and other elements show tremendous promise for breakthrough performance in gas storage. Enough progress has been made by the HSCoE that it may be possible to use sorbents to construct a hydrogen storage system that meets DOE's 2010 targets. The capabilities of these materials can be

improved further by developing a better understanding of both the factors governing their performance and the design principles for synthesizing the materials and constructing the required systems.

The HSCoE developed reversible sorbent materials for energy storage within this DOE Fuel Cells Technology Project. The HSCoE developed the science base and technology advances needed to identify and create nanostructured sorbents that have the potential meet DOE goals for on-board storage. A guiding principle in developing the required materials was that a continuum of energies exists for binding to substrates and molecules. On the weak side of the continuum is non-dissociative physisorption due purely to van der Waals (vdW) forces (4 kJ/mol). On the strong side is the full chemical bond in materials such as methane (with an energy of ~400 kJ/mol). Between these two limits, with binding energies between 10 and 40 kJ/mol, are: (i) stronger physisorption (due to modification of the key parameters affecting vdW forces), (ii) dihydrogen binding via the formation of complexes that exhibit bond stretching and joint charge transfer interactions, and (iii) weak, reversible chemical bonding of mono-atomic hydrogen to strained receptor materials (“spillover”). The DOE goals can be met with sorption-based materials if (i) the energy for adsorption can be designed to be in an optimal range (10–40 kJ/mol) [2], and (ii) efficient volumetric arrangement of a sufficient number of suitable binding sites can be achieved with a low-weight material. These goals are difficult to reach in conventional high surface area adsorbents that are limited by low physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, and excessive macroporosity and poor volumetric packing.

Approach

The HSCoE discovered the limits of performance of high surface area adsorbents and synthesized and tested sorbents with the potential to meet the DOE system targets for reversible storage. This involved the design and synthesis of new materials that bind large amounts of hydrogen on both a per-weight and a per-volume basis as (i) weakly and reversibly bound atoms and/or (ii) strongly bound molecules. The HSCoE focused on determining binding mechanisms and energies, and the manner in which suitable sites could be organized in space to achieve a high-volumetric density using low-weight frameworks. This involved determining the affects of geometry, introduction of defects, adventitious dopants, and catalytic species, as well as elemental substitution. The HSCoE investigated a range of different lightweight nanomaterials and porous frameworks and championed the development of new sorbents for ambient temperature hydrogen storage.

Results

HSCoE members worked closely together to effectively leverage unique partner capabilities in a coordinated set of focused efforts to accelerate storage materials development. These close and actively coordinated interactions resulted in dozens of joint projects in the past year, in which the rapid materials development is illustrated by the more than 20 joint publications. In addition, the HSCoE works with more than 40 groups from around the world and directly with the chemical hydride, metal hydride, and engineering centers of excellence to ensure that our development efforts leverage other research activities for efficient utilization of resources. Finally, the HSCoE also ensures that its development efforts are transparent and provided to the scientific community in a timely manner to again help speed the storage materials' development progress. This is done through the active organization by HSCoE partners of hydrogen storage materials conferences around the world, and through more than 100 presentations at conferences and more than 50 publications in refereed journals in the past year. A few highlights of results from the massive amount of development work from throughout the HSCoE are provided in the following.

Optimizing High SSA Materials: In general, storage capacities increase with higher SSAs and higher bulk densities. However, while these are necessary requirements for high storage capacities, enhanced binding energies for the entire capacity range will be required in order for the materials to be used to meet DOE targets. The HSCoE has focused efforts to improve all of these material properties independently and simultaneously. Within the last year, the HSCoE

continued to increase specific surface areas and capacities of materials using coordinated framework and porous carbon materials (Figure 1). The HSCoE used a number of different synthetic routes to form optimized geometric materials using processes that include: templating, graphene, aerogel, chemical, vapor, and/or pyrolysis. Even though most of these materials will require cryocompression, they have no significant heat transport issues, can operate at moderate pressures, and may require the least engineering (compared to metal or chemical hydrides) to design and construct a system that could meet the DOE 2010 targets. Material capacities of more than 7 wt% and 40 g/L have been demonstrated at 77 K. These capacities increase by ~30% if the sorbent system stored hydrogen at ~50 K, i.e. >8 wt% and >50 g/L. At this temperature, only ~20 bar pressures would be required and it may be possible to design a storage system that could meet the DOE 2015 hydrogen storage capacity targets. This increase in capacity would be traded against decreases in well-to-fuel cell efficiencies but could improve overall system cost compared to high pressure (i.e. 350 to 700 bar) storage by using much lower pressures (Figure 2).

Improving Site-Specific Dihydrogen Binding Energy:

In addition to optimizing geometric structures to improve storage properties, the HSCoE pioneered the use of multiple-element materials to improve dihydrogen binding. In good agreement with theoretical models [3], B substituted with an sp² structure in carbon enhances hydrogen binding to ~11 kJ/mol [4]. Over the past year, the HSCoE also demonstrated this enhanced hydrogen binding in B substituted carbons through the use of neutron scattering and diffuse reflective infrared fourier transform spectroscopy (DRIFT) (see PSU and NIST contributions to this report). The main issues

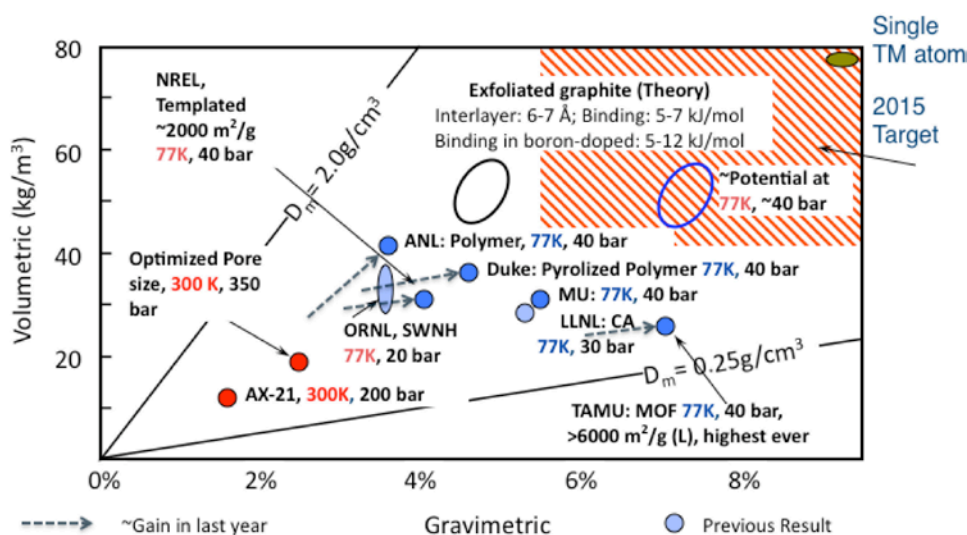


FIGURE 1. Plot of Gravimetric versus Volumetric Capacities Showing Progress over the Last Year for High SSA Materials

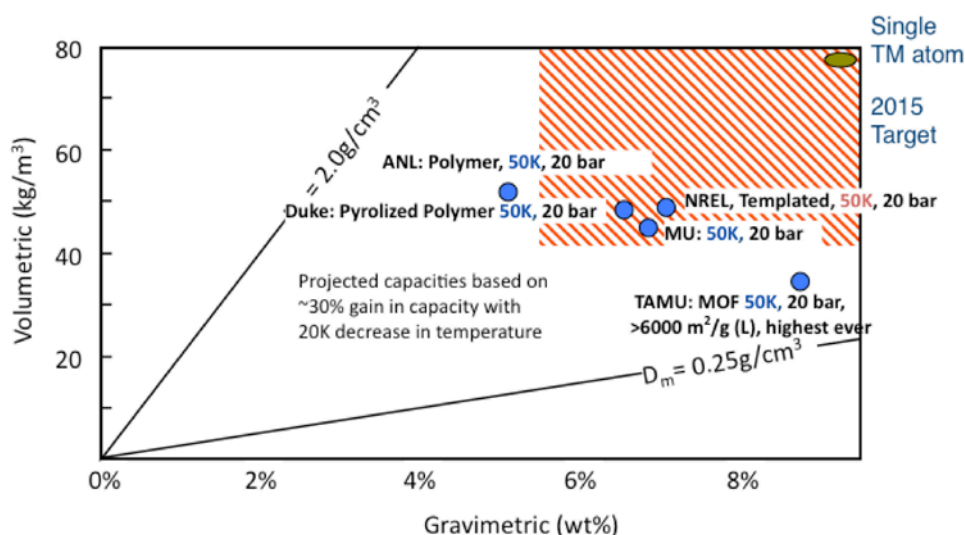


FIGURE 2. The capacities of high specific surface area materials increase by $\sim 30\%$ at 50 K compared to 80 K. This means that sorbents may meet DOE 2015 capacity targets at ~ 50 K and ~ 20 bar. These increased capacities need to balance system cost and efficiency. However, storage system costs will be significantly lower at 20 bar, compared to 350 or 700 bar, while well to tank efficiencies will be lower by about 10% compared to 350 bar storage.

remaining include the need to substantially increase the B concentration while maintaining a high SSA (see PSU and NREL contributions to this report). In this regard, the HSCoE investigated the use of several synthetic techniques to address these issues, including: pyrolysis of BC precursor materials, templating BC_3 , and chemical replacement processes.

In addition to B enhancing dihydrogen binding and thus storage capacity at near-ambient temperatures, B and N have also been used to stabilize single-metal centers and metal clusters on high surface area materials. The HSCoE has championed the use of coordinated metal centers to increase dihydrogen binding and to also enable multiple dihydrogen binding at a single adsorption site. Work by TAMU and NIST have demonstrated the enhanced binding of metal centers in metal organic framework materials. Furthermore, the neutron scattering work confirm the theoretical prediction that the binding energy depends on the metal used.

Furthermore, some of these materials can bind multiple hydrogen molecules to a single metal center where the heats of adsorption are in the optimized range for the entire capacity (Figure 3 [5]); decreasing the engineering required while increasing the capacity. Although initial reaction to these materials was skeptical, recent experimental results validate the predictions, and there is good agreement between the predictions and all known 3-d metal center materials. Over the past year, the HSCoE has focused efforts in identifying materials and processes that are more synthetically possible (e.g. Figure 4, [6]) starting from existing materials. These types of materials provide a reasonable path for meeting

DOE's ultimate storage targets (i.e., 7.5 wt% and 70 g/L) with inexpensive sorbents.

Improving Spillover Material Processing: While most of the work within the HSCoE is associated with enhancing the storage of molecular hydrogen, we are also developing materials that can reversibly store weakly bound hydrogen atoms. For example, Ralph Yang's group at the University of Michigan pioneered the use of spillover as a viable high capacity ambient-temperature hydrogen storage process. UM demonstrated that over 4 wt% hydrogen can be reversibly stored on a catalyst containing metal organic framework material, and calculations indicate that 7–8 wt% (50–60 g/L) should be achievable at ambient temperature. Over the past year, the HSCoE continued developing new spillover based materials including demonstrating the spillover is enhanced on pyrolyzed sucrose; a material often used to bridge between catalysts and high surface area receptors. In addition to improving catalyst processing, receptor materials, reproducibility, and rates, the HSCoE also identified potential mechanisms based on geometrical structures and electronic properties that substantially reduce the barrier to diffusion and thus could significantly increase the kinetic transport rate of atomic hydrogen on the receptor surfaces.

Conclusions

- The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. This

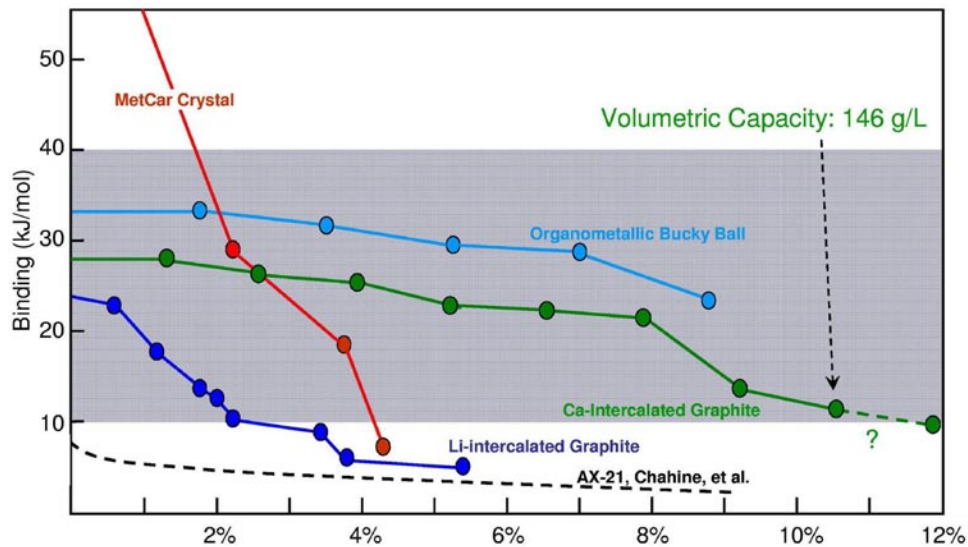


FIGURE 3. Some coordinated metal center materials designed by the HSCoE maintain optimum hydrogen binding energies for their entire capacity range. This helps engineering and enhances the material capacity.

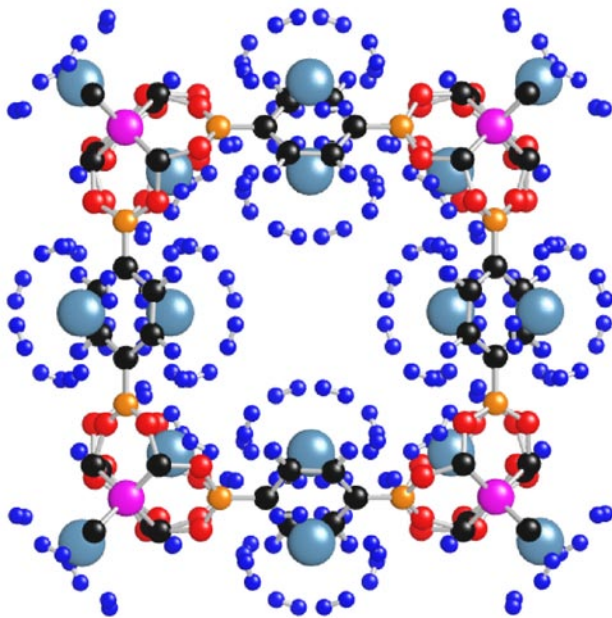


FIGURE 4. Covalent-organic framework with Ca atoms integrated on carbon linkers. This is an example where known materials were used to form sorbents with a potential for high hydrogen storage capacities.

resulted in the development of multiple new materials that may be able to be used to meet the 2010 and possibly the 2015 DOE storage system targets including cost and gravimetric/volumetric capacities.

- Designed/developed substituted materials to enable higher hydrogen binding energies in porous materials. Confirmed the enhanced hydrogen binding of the B substituted materials with neutron scattering and DRIFTS measurements. BC_x materials could increase the storage tank temperature and capacity, thus reducing overall system costs once sufficient B concentration and specific surface area are achieved. Substituted materials also enhance stabilization of metals and potentially improve weak chemisorption processes.
- Developed new materials with stronger H_2 binding either through interactions with exposed metal centers or electrostatic effects. This work included the experimental validation by neutron scattering that the binding energy depends upon the specific metal used. The Center also identified materials that could be more easily synthesized. This work paves the way to meet DOE's ultimate storage targets with ambient temperature storage densities greater than liquid H_2 .
- Improved spillover process understanding to help create sorbents with higher capacities and sorption rates that can meet DOE 2015 hydrogen storage targets at ambient temperatures. This included identification of electronic and structural dependencies for atomic hydrogen diffusion on the receptor materials, the thermodynamic processes of the catalysts, and improved spillover rates and capacities with functionalization.
- HSCoE works with dozens of groups and provides leadership throughout the world.

Future Directions

The HSCoE will focus the remaining effort on completing a comprehensive final report. Provide DOE with a comprehensive review of all significant work done, results, lessons learned, and recommendations for future sorption materials development. Key aspects of this review will include material and/or process recommendations for future consideration in engineering system analysis, design, and demonstration, as well as future research and development efforts, including:

- The Center recommends that development efforts for specific material classes be continued where viable routes exist for synthesizing sorbents that can be used to meet the appropriate set of targets:
 - The specific selection criteria for future efforts should focus on the DOE 2015 and the ultimate full-fleet hydrogen storage targets.
 - Numerous materials recommended for no further development.
- Develop materials for hydrogen storage by weak-chemisorption:
 - Ambient-temperature storage via catalytic hydrogen dissociation and transfer to high SSA receptor materials (e.g., spillover) demonstrate 10 to 30 kJ/mol reversible hydrogen binding energies, which enable ambient-temperature storage.
 - Minimizes thermal management and reduces overall storage system cost.
 - Need to improve understanding of atomic H transport to increase rates/capacities and enhance reproducibility and durability.
 - Weak chemisorption enables ambient temperature storage with systems having more than 75% of the material capacities at moderate (~100 bar) pressures.
- Develop materials for multiple hydrogen storage on designated sites:
 - Maybe only route that enables materials to be developed to meet DOE ultimate system targets; especially for on-vehicle refueling.
 - Inexpensive material systems identified to meet ultimate targets.
 - Meeting DOE's ultimate targets will enable hydrogen to become a viable energy carrier for transportation and other important renewable energy applications.
- Develop substituted/heterogeneous materials that have demonstrated hydrogen binding energies in the range 10–25 kJ/mol:
 - Enables near-ambient-temperature (150–250 K) hydrogen storage.
 - These heterogeneous materials also demonstrate substantial stabilization of single-metal centers and other absorbed species that improve hydrogen storage.
- Limit development of materials in which the storage mechanism is physisorption to only those with optimized structures:
 - To meet the DOE 2015 targets, the only physisorption materials that should be considered for development are those that can have SSAs greater than ~3,000 m²/g, optimized uniform pore sizes in the range of ~0.7 to ~1.5 nm, and excess material hydrogen storage capacities greater than 50 g/L and 7 wt% at cryogenic temperatures (~80–200 K) and moderate pressures (less than 100 bar).

Remaining Issues:

- Develop robust, reproducible, and scalable synthetic methods that create materials where all the adsorption sites are accessible to the hydrogen.
- Improve computational methods to more accurately predict the ability to synthesize designed materials and the hydrogen storage capacity as a function of temperature and pressure.
- Develop a better understanding of atomic hydrogen transport on receptor materials.
- Develop a better understanding of metal center coordination and its effect on hydrogen adsorption.
- Develop materials in concert with designs for hydrogen storage systems.
- Develop sorbent material measurements standards and certifications.

Support the Hydrogen Storage Engineering Center of Excellence (HSECoE): Work with the HSECoE to select potential materials and provide their intrinsic hydrogen storage properties needed for system engineering design, analysis, and perhaps demonstration.

Sorbent Materials Approach to DOE 2010 Targets: In general, sorbents meet almost all of the DOE hydrogen storage targets. As discussed above, sorbents may greatly improve volumetric capacities, and the HSCoE has developed several materials that may meet DOE's 2010 on-board refueling targets.

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