

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

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in the tank with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Work is directed at overcoming barriers to DOE system goals and identifying pathways to meet the hydrogen storage system targets. In particular, the HSCoE strives to:

- Develop high-specific-surface-area sorbent materials 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 are organized in focused groups to optimize development and avoid duplication of effort, with seamless integration of experiment/theory.
 - Quantitative down-select criteria are used prior to beginning research and development and at Go/No-Go points.

Technical Barriers

The HSCoE is developing novel high-surface-area hydrogen storage materials for advanced fuel cell technologies. The HSCoE presently has 15 active projects at 18 institutions. HSCoE partners are conducting a wide range of applied research and engineering studies on currently available sorbent materials and developing design principles and synthetic methods for next-generation materials that will meet the critical DOE system hydrogen storage targets. The technical barriers addressed by these projects from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan include:

Objectives

The Hydrogen Sorption Center of Excellence (HSCoE) seeks to discover and develop high-capacity sorbent materials that can operate at ambient temperatures and be efficiently and quickly charged

General:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management

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

Reversible On-Board:

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

Accomplishments

The HSCoE partners work closely together to systematically accelerate the development of advanced hydrogen sorbent materials. For specific details, please review their individual contributions to this report. A summary of representative accomplishments is listed as follows.

- The HSCoE partners work in close coordination performing focused development of hydrogen storage materials. The coordination activities included:
 - Materials-development selection criteria were created for different materials classes to provide guidance regarding whether a given development effort should proceed.

Technical Targets

The HSCoE is developing sorption materials for hydrogen storage systems. As shown in Table 1, the HSCoE is focused on addressing the higher-risk targets for sorbents that are associated with capacity and costs, including:

TABLE 1. Status of Sorption Materials' Ability to Meet DOE System Storage Targets

Storage Parameter	Units	2010	2015	Ultimate
System Net Gravimetric	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	1.8 ^M (0.055)	2.5 ^H (0.075)
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	0.9 (0.028)	1.3 ^M (0.040)	2.3 ^H (0.070)
Storage System Cost (and fuel cost)	\$/kWh net (\$/kg H ₂) \$/gge at pump	4* (133) 2-3	2* ^M (67) 2-3 ^M	TBD ^H 2-3 ^H
Durability/Operability				
• Operating ambient temperature	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Cycle life (1/4 tank to full)	Cycles	1,000	1,500	1,500
• Cycle life variation	% of mean (min) at % confidence	90/90	99/90	99/90
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	atm (abs)	4FC/35 ICE	3FC/35 ICE	3FC/35 ICE
• Max delivery pressure from storage system	atm (abs)	100	100	100
Charging/Discharging Rates				
• System fill time (for 5-kg H ₂)	min (kg H ₂ /min)	4.2 min (1.2 kg/min)	3.3 min (1.5 kg/min)	2.5 min (2.0 kg/min)
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20°C)	s	5	5	5
• Start time to full flow (-20°C)	s	15	15	15
• Transient response 10%-90% and 90% -0%	s	0.75	0.75	0.75
Fuel Purity (H ₂ from storage)	% H ₂	99.99 (dry basis)		
Environmental Health & Safety		Meets or exceeds applicable standards		
• Permeation & leakage	scc/h			
• Toxicity	-			
• Safety	-			
• Loss of useable H ₂	(g/h)/kg H ₂ stored	0.1	0.05 ^M	0.05 ^M

*The storage system costs are currently under review and will be changed at a future date.

Unmarked: low risk, high probability to meet; M: medium risk, medium probability to meet; H: high risk, low probability to meet.

TBD - to be determined.

- Technology development “roadmaps” were updated to reflect progress toward addressing DOE’s Multi-Year Research, Development, and Deployment Plan.
- The HSCoE is completing a materials Go/No-Go recommendation document that will feed into the final report for the center.
- The HSCoE developed and applied advanced and new spectroscopic techniques to determine the relationships between material structure and hydrogen storage behavior.
- NIST determined bulk elemental compositions of materials of interest to the HSCoE using prompt gamma analysis, and employed inelastic neutron-scattering methods to determine the location of hydrogen-binding sites and the site-specific hydrogen adsorption strength in several different materials. Materials studied included metal-decorated, carbon-based materials; metal organic frameworks (MOFs); and boron-infused carbon materials. This understanding helps to speed sample development and material synthesis aimed at reaching the DOE targets.
- NIST illustrated the site-specific hydrogen adsorption strength in MOF materials. The overall appreciation of this determines the isosteric heats of hydrogen adsorption. The size and shape of the Coulomb potential determines inelastic neutron-scattering features. Spectra are composed of rotations and multiple rotation-phonon transitions.
- UNC performed ^1H nuclear magnetic resonance (NMR) and ^{11}B NMR spectroscopy to evaluate the porosimetry of materials using H_2 as the probe molecule, and also to evaluate boron site symmetry in various boron-substituted materials. UNC demonstrated unexpectedly large crystal fields promoting strong binding and/or trapping to produce high H_2 capacity in MOFs. UNC determined that the nature of activated polyether ether ether ketone (PEEK)-adsorbing surfaces remains unchanged even for material with the highest burn-off value. UNC also determined that opened single-walled nanohorn (SWNH) materials confine H_2 in an interconnected space composed of interstitial and endohedral sites. Adsorption occurs predominantly in the interstitial volume at low pressure with the endohedral volume being filled with increasing pressure.
- NREL improved and increased hydrogen storage materials’ instrumentation to perform more than 200 measurements on materials from external sources and more than 1,000 measurements all together.
- The HSCoE dedicated significant effort and made substantial progress on spillover.
 - UM demonstrated that oxygen surface functionalities and adsorbed molecules from gaseous impurities (such as methane) in H_2 can enhance spillover. In addition, UM identified that Ti and V chlorides improve catalysts functions.
 - NREL identified that barriers to migration are lowered sufficiently to enable spillover via structural features, electric perturbations, and/or quantum mechanical tunneling where H will diffuse before it desorbs.
 - NREL developed new catalyst processing that improved spillover capacity and charging rates. This includes the observation that B-substituted receptor materials enhance spillover performance. NREL also identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements.
 - Rice calculated that B and N provide good anchors for metal spillover catalysts, and that N-doping may enhance spillover kinetics. Furthermore, Rice calculated that the barrier for H to move from the metal catalyst to the hydrogenated phase is very small and can be overcome at room temperature.
 - Caltech synthesized 3-gm batches of Pt-loaded super-activated carbon for spillover analyses. Caltech investigated the effect of sample size on the measurements to observe spillover and concluded that some of the inconsistencies in the data may be related to small sample sizes.
- The HSCoE synthesized and characterized several types of new, promising hydrogen sorption materials.
 - ANL and University of Chicago synthesized and characterized over 50 different structures in three classes of polymers. Polymers with specific surface areas as high as $\sim 1,900 \text{ m}^2/\text{g}$ and tunable pore size from 0.6 to 0.9 nm were prepared. Excess H_2 sorption of 5.1 wt% at 77 K (40 bar) and material bulk densities of $\sim 1.4 \text{ g/ml}$ were achieved with virtually no loss in storage capacity.
 - Caltech synthesized intercalated graphite materials that maintain constant isosteric heats of adsorption for their entire capacity range. The isosteric heat in KC24, RbC24, and CsC24 is 9, 11, and 13 kJ/mole H_2 , respectively, and unlike most other physisorbents where the heats decay as a function of loading, the values from intercalated graphites are generally constant as a function of loading.

- Texas A&M University synthesized 50 new ligands for MOF formation and evaluated the contribution to hydrogen adsorption from catenation in MOFs. Also, the effect of a variety of MOF open metal centers and double-bond-containing ligands on hydrogen affinity was studied. In addition, TAMU discovered a general way to construct MOFs by incorporating mesocavities with microwindows to create materials with extremely high specific surface areas. Materials with the highest specific surface areas ever produced (over 9,000 m²/g) were synthesized.
- LLNL worked in collaboration with Metal Hydride Center of Excellence members at HRL Laboratories to develop novel carbon aerogels with large pore volumes and containing dispersions of carbon nanotubes as scaffolds for CA/LiBH₄ nanocomposites. These materials showed a decrease in hydrogen desorption temperature relative to bulk LiBH₄. In addition, aerogels containing functional groups capable of binding and stabilizing organometallic species were synthesized to provide absorption sites for single-metal centers that provided enhanced dihydrogen binding.
- Duke developed thermal treatments of PEEK materials with high specific surface areas (>3,000 m²/g), high microporosity, higher binding energy (8.1 kJ/mol), and >6 wt% at 77 K, 20 bar with a projected 42g/L volumetric capacity. Complementary H₂-NMR measurements showed >6 wt% storage at 120 K and 10 MPa. Also developed methods for successfully doping these high-surface-area porous carbons with variable amounts of B and Pd.
- PSU and NREL demonstrated that incorporation of boron into nanoporous carbon frameworks improve isosteric heats of adsorption for hydrogen to 11–15 kJ/mol and were able to increase boron concentrations in porous materials to ~15%. In addition, boron-substituted carbon demonstrated improved metal integration for stronger dihydrogen storage as well as improved spillover. The enhanced binding energy is sufficient to store substantial hydrogen within the DOE target temperature range of ~220 to 350 K.
- NREL developed novel, scalable, synthetic processes, such as templating, to form high-surface-area lightweight materials with optimum pore structure and composition for H₂ storage. This included the ability to form BC_x materials that have shown great promise for stabilizing single-metal centers for enhanced dihydrogen storage and for improving metal catalysts for spillover.
- ORNL synthesized SWNHs with tunable small pores in gram quantities, which is a scalable production rate. Short, opened SWNHs reversibly store significant hydrogen at room temperature (1.5 wt% at 100 bar). These “nanoengineered pores” are defined by both the unique nanostructure self-assembled during synthesis and the activated pores during oxidation.
- ORNL developed methods to produce uniformly vapor-deposited Ca to attempt to form enhanced binding due to induced charge separation. Theoretical predictions suggest that Ca and Sr should coat C nanostructures without clustering while providing sufficient electric field strength to polarize and bind H₂ with 8.4 wt% and 0.4 eV for Ca.
- Rice produced graphene-nanoribbon scaffolds as H₂ storage slit-pore materials using scalable industrial-type spinning processes. In addition, a dynamic multilayer adsorption concept using electrostatic enhancement for H₂ storage was investigated.
- APCI enhanced its experimental capabilities to allow the use of pure fluorine for the synthesis of graphene-intercalated compounds. First-stage graphene-intercalated compounds containing fluoride anions were prepared using pure F₂ and were characterized for hydrogen storage capacity and heat of adsorption. In addition, new synthetic strategies for the preparation of high-surface-area, templated, boron-substituted carbons were developed.
- On top of those already mentioned, the HSCoE made several important accomplishments in the area of theory and modeling.
 - At APCI, predictive computational modeling revealed that crystalline BC₃ is an attractive target material for hydrogen storage. Unlike graphite, chemisorption of hydrogen by BC₃ provides a chemical driving force for H₂ penetration into the lattice. The energies of hydrogen diffusion of chemisorbed hydrogen in BC₃ were calculated, showing that hydrogen diffusion on the surface is unlikely at moderate temperatures. Although the bond dissociation energies of chemisorbed hydrogen in BC₃ suggest that hydrogen binding may be irreversible at high levels of hydrogenation, APCI's computational modeling suggests a path forward by incorporating substitutional nitrogen atoms in the lattice. The average absorption energies for materials that incorporate nitrogen are significantly lower.
 - At NREL, theory and experiment continued to iteratively interact to design and synthesize

several new H₂ storage materials. This included validating the initial theoretical prediction to experimental Ti-silica results from the University of Windsor of single-metal atoms dispersed and stably supported on a matrix being able to reversibly hold more than 2 H₂. These calculations also revealed the unique properties of inexpensive Ca to make hydrogen storage materials with very viable synthetic routes. These revolutionary new Ca materials could store H₂ at >100 g/L and >10 wt% (much higher than liquid hydrogen) at ambient temperatures, offering the potential to exceed DOE's ultimate system targets including cost and volumetric/gravimetric capacities.

- Rice performed Grand Canonical Monte Carlo simulations to optimize the storage in 3-dimensional foams. The specific surface areas of foams were evaluated and quantum corrections were incorporated to estimate realistic storage capacities. Hydrogen uptakes in metallacarboranes were also studied.



Introduction

To realize the full energy efficiency, energy savings, and environmental improvements that fuel cells can provide, significant improvements over currently available gas storage technologies are required. The storage targets presented in DOE's Multi-year Research, Development and Demonstration Plan for Fuel Cell Technologies state the critical needs and goals. At this time, no known storage system can meet the mass, volume, cost, safety, and efficiency requirements for vehicular or early market storage systems. Consequently, DOE is investigating solid-state storage options such as metal hydrides, chemical hydrides, and sorbent materials. Nanostructured high-surface-area materials containing carbon, metals, oxygen, and other elements show tremendous promise for breakthrough performance in gas storage. However, the capabilities of these materials can be improved 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 is developing reversible sorbent materials for energy storage within the U.S. DOE Fuel Cells Technology Project. The HSCoE is developing the science base and technology advances required to meet DOE goals for on-board storage by researching a range of nanostructured adsorbents. A guiding principle in developing the required material is 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 50 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 (10–50 kJ/mol) [1], 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 main goals of the HSCoE are to discover the limits of performance of high-surface-area adsorbents and to synthesize and test sorbents that can be used to meet the DOE system targets for reversible storage. This involves the design and synthesis of 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 focuses on determining binding mechanisms and energies, and the manner in which suitable sites may be organized in space to achieve a high-volumetric density using low-weight frameworks. This involves determining the affects of geometry, introduction of defects, adventitious dopants, and catalytic species, as well as elemental substitution. The HSCoE currently investigates a range of different lightweight nanomaterials and porous frameworks. In addition to the current materials systems being studied, the HSCoE strives to be nimble, flexible, and responsive to incorporating promising new ideas, materials, and concepts as they arise.

Results

HSCoE members work closely together to effectively leverage unique partner capabilities in a coordinated set of focused efforts to accelerate storage materials development. This close and actively coordinated interaction has resulted in more than 40 joint projects in the past year, in which the rapid materials development is illustrated by the more than 30 joint publications. In addition, the HSCoE works with more than 40 groups from around the world and directly with the chemical hydride and metal hydride 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 110 presentations at conferences and more than 90 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 below.

Optimizing High-Specific-Surface-Area Materials

In general, storage capacities increase with higher specific surface areas 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. Recently, a tremendous amount of progress has been made on increasing specific surface areas of materials using coordinated framework and porous carbon materials. Material capacities of ~7 wt% have been demonstrated. The HSCoE is pursuing 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.

Within the HSCoE this year, Hongcai Zhou's group at TAMU developed a number of MOFs with record amounts of specific surface area, including one with over 9,000 m²/g (Langmuir). These materials have yet to be characterized for their hydrogen storage properties, but the interconnected matrix used to form these materials offers the potential for better optimized pore sizes, as compared to other MOF materials. Furthermore, Di-Jia Liu's group at ANL demonstrated that, unlike heterogeneous pore size materials (e.g., activated carbon), their polymer materials with small (i.e., less than 1 nm) uniform pore sizes can be compressed to form materials with ~1.4 g/ml bulk densities without significant loss of gravimetric hydrogen storage capacity. As shown in Figure 1, if bulk densities close to this can be achieved with 6 to 7 wt% hydrogen storage materials, then volumetric capacities surpassing those of liquid nitrogen (i.e., 70 g/L) could be achieved at a much higher temperature. This will dramatically reduce

system and delivery costs. Finally, Channing Ahn's group at Caltech synthesized stage I intercalated graphite structures (Figure 2) to demonstrate that materials with uniform and small (i.e., 0.5 to 0.6 nm) pore size or wall spacing result in binding energies that remained constant for the full capacity range. These results also demonstrate clearly that smaller spaces increase binding energy, with ~13 kJ/mol being observed for Cs

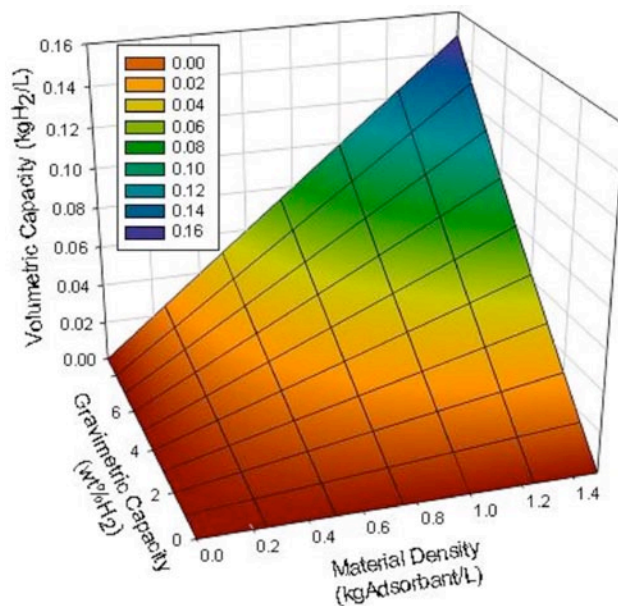


FIGURE 1. Plot of the volumetric-capacity dependence on material density and gravimetric capacity.

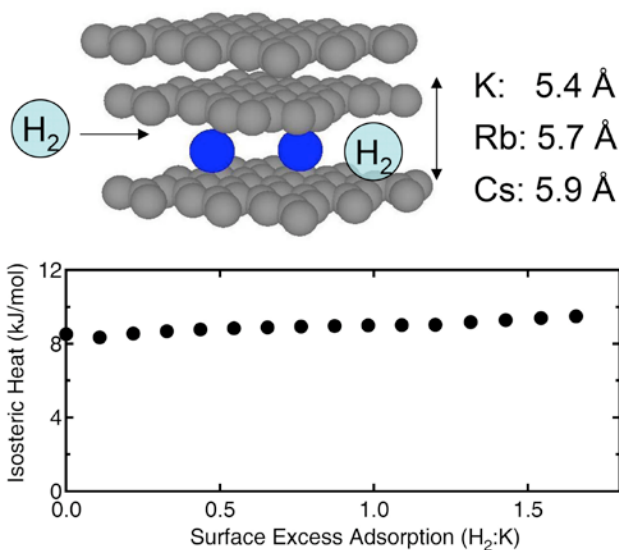


FIGURE 2. Schematic of stage I intercalated graphite materials and the measured binding energies of K-intercalated graphite, which stays constant for the entire range of capacity.

intercalated graphite. The experimental data indicate that at this binding energy, a substantial amount of the capacity still remains at ~200 K. All of these noteworthy results from the HSCoE partners demonstrate viable pathways to creating sorbent materials that may operate at cryocompressed conditions, but may be used to meet DOE targets.

Improving Site-Specific Dihydrogen Binding Energy

In addition to optimizing geometric structures to improve storage properties, the HSCoE has pioneered the use of multiple-element materials to improve dihydrogen binding. In good agreement with theoretical models [2], B substituted with an sp^2 structure in carbon enhances hydrogen binding to ~11 kJ/mol [3]. The main issues remaining include the need to substantially increase the B concentration while maintaining a high specific surface area (see PSU and NREL contributions to this report). In this regard, the HSCoE is investigating the use of several synthetic techniques to address these issues, including: pyrolysis of BC precursor materials, templating BC_3 , and chemical replacement processes. Similarly, APCI (see their contribution in this report) is investigating the use of F to enhance dihydrogen binding.

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. NREL has championed the use of coordinated metal centers to increase dihydrogen binding and to also enable multiple dihydrogen binding at a single adsorption site. Furthermore, some of these materials bind dihydrogen in the optimized range for the entire capacity (Figure 3), which decreases the engineering required while increasing the total storage 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. Recently, substantial amounts of work identified the unique properties of Ca for hydrogen storage [4,5]. ORNL's work indicates that the interactions between Ca and carbon matrices is sufficient to prevent Ca agglomeration; enabling single metal atoms to be maintained for multiple dihydrogen adsorption at each Ca atom. As discussed in the NREL contribution to this report, Ca coordinated in the correct way can reversibly store over 100 g/L and 10 wt% at ambient temperatures (Figure 4). This is substantially higher than liquid hydrogen, but at ambient temperature. Based on initial calculations from ANL, storage systems at ~75% of the material capacities should be achievable under these conditions. Thus, these inexpensive Ca-based hydrogen storage materials provide a reasonable path for meeting DOE's ultimate storage targets (i.e., 7.5 wt% and 70 g/L).

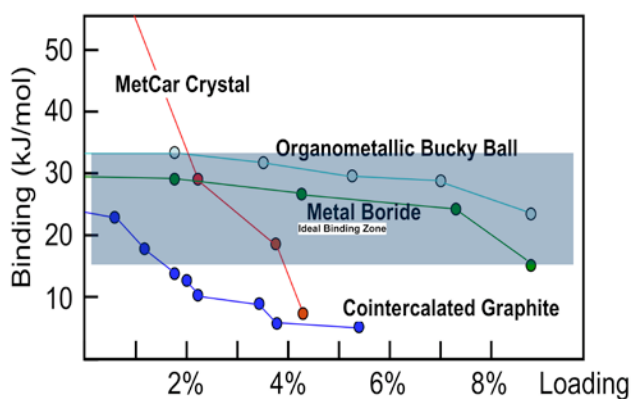


FIGURE 3. Some coordinated metal center materials maintain optimum hydrogen binding energies for their entire capacity range. This helps engineering and enhances the material capacity.

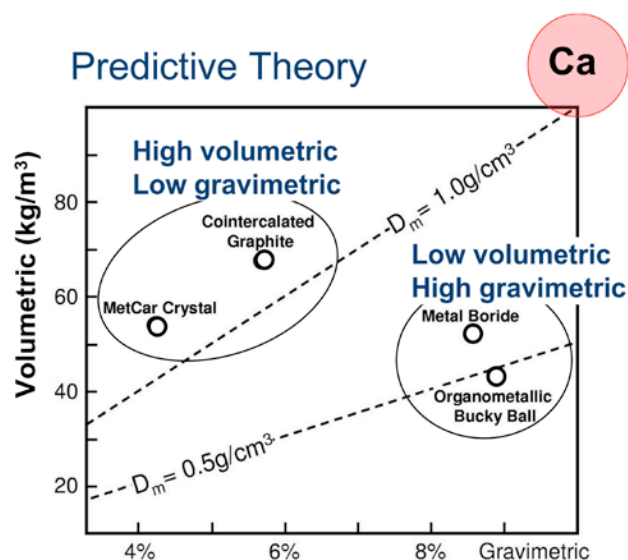


FIGURE 4. Plots of predicted material capacities for different coordinated metal materials. Ca-based materials have the potential to exceed all of them and to be used to meet DOE's ultimate targets.

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 MOF material, and calculations indicate that 7–8 wt% (50–60 g/L) should be achievable at ambient temperature. In addition, analysis from ANL indicate that systems using spillover materials could have ~75%

of the material capacities, suggesting that the DOE 2015 targets of 5.5 wt% and 40 g/L could be achieved with an optimized spillover material. Thus, the HSCoE has several partners including UM investigating the different components of spillover and improving materials synthesis to resolve the remaining issues associated with reproducibilities, capacities, refill rates, and costs. Initial work validated the thermodynamics of the spillover processes and broadened the breadth of materials that demonstrate spillover. In the past year, work at NREL and Rice University developed a better understanding of how the hydrogen moves from the catalyst to the receptor and then also along the receptor. With this understanding, the HSCoE can guide development efforts to improve material performance further. In addition, UM and NREL identified a number of ways to improve catalytic and receptor material performance. However, NREL also identified several issues that contribute to batch-to-batch and lab-to-lab irreproducibilities in the materials processing, and the fact that the effluent gas needs to be actively monitored to ensure that undesired chemical reactions with surface functional groups is not occurring.

Conclusions

- The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. This resulted in the development of multiple new materials that may meet the 2010 DOE storage system targets including cost and gravimetric/volumetric capacities.
- Designed/developed substituted materials to enable higher hydrogen binding energies in porous materials. Demonstrated higher B concentration (10%–15%) in carbon with higher surface areas (800 m²/g). BC_x materials could increase the storage tank temperature and capacity, thus reducing overall system costs.
- Developed new materials with stronger H₂ binding either through interactions with exposed metal centers or electrostatic effects. This work paves the way to meet DOE's ultimate storage targets with ambient temperature storage densities greater than liquid H₂.
- Identified new material processes that increase sorption rates and hydrogen storage capacity by >15% at room temperature.
- Improved spillover kinetics understanding enables materials to be designed with higher capacities and sorption rates that can meet DOE 2015 targets. Identification of hole-induced improvements along with receptor catalytic properties points toward inexpensive spillover material with fast sorption.
- HSCoE has dozens of collaborative interactions that are openly discussed, evaluated, and redirected during face-to-face meetings and with Webcasts either in small groups or by the whole center.
- HSCoE works with dozens of groups and provides leadership throughout the world.

Future Directions

- **Focused Materials Development:** Wrap up focused materials development work and complete materials characterization and validation. Maintain awareness of advances made in different focused development efforts and other groups, to ensure efficient coordination of efforts.
 - **Porous materials:** Develop high-surface-area materials with optimized pore structure for efficient volumetric capacities and enhanced hydrogen binding. Integrate substituted elements (e.g., boron in porous carbons) produced by scalable processing (e.g., templates, propped graphenes, carbon and non-carbon aerogels). Work interactively to characterize the structural properties, analyze the optimal pore effect, and investigate the highest potential for H storage for different sorption mechanisms. Leverage carbon-based materials' experience to determine if other light elements can be used to implement mechanisms more straightforwardly, or if brand new, more desirable approaches may be found.
 - **MOF Materials:** Further enhance H₂-MOF interactions by preparing materials with a higher density of coordinatively unsaturated metal centers, improve H₂ uptake at temperatures higher than 77 K by ligand and MOF design, and increase MOF thermal stability while maintaining its porosity. Increase volumetric performance using denser H₂ packing and optimal pore sizes.
 - **Metal-Decorated Structures:** Focus on tractable processing with identification of atomic structures, characterize the reactions, simulate their H-storage properties, and improve the properties.
 - **Spillover Materials:** Work in well-coordinated groups to develop improved understanding of spillover processes and reproducible materials processing. This includes determining the contributions of bridges and receptors to kinetic limitations, thermodynamically acceptable configurations, and the roll catalyst/receptor integration plays. Also, scale materials processing to the multiple (tens)-gram scale for validation and system testing. Perform very high-pressure measurements (>100 bar) to determine saturation capacities.
 - **Integrate Theory and Experiment:** Iterative, close interactions in the HSCoE have

already taught theoreticians what is possible experimentally, and *vice versa*. Continued work at this interface will increase the rate of discovery and synthesis of viable materials.

- **Materials Down-Select:** After down-selecting, allocate resources focused on completing work on selected materials to demonstrate their potential to meet DOE 2010 and 2015 system targets and to provide performance properties for system design. Also, identify potential cost-effective and scalable processing that will produce the hydrogen storage materials with access to the high density of enhanced binding energy sites.
- **Provide Recommendations:** Provide DOE with a comprehensive review of all significant work done, results, lessons learned, and recommendations for future sorption materials development in a report and publication. 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.
- **Support 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 HSECoE has developed several materials that may meet DOE's 2010 on-board refueling targets.

References

1. S.K. Bhatia, A.L. Myers, *Langmuir* 2006, 22, 1688.
2. e.g., Kim et. al., *PRL* 96, 016102 (2006).
3. e.g., Chung et al., *JACS Comm.* (2008), PSU & APCI AMR 2009.
4. Y-H Kim, et al., *PRB* 2009, 79, 115424. submitted in 2007.
5. M. Yoon, et al., *Phys. Rev. Lett.* 2008, 100, 206806.