

## IV.C.1e NREL Research as Part of the Hydrogen Sorption Center of Excellence

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hydrogen binding energy in the range of 15–20 kJ/mol (for room temperature operation).

- Decrease heat-transfer requirements to increase on-board refueling times.
- Sorption materials typically meet DOE refueling and delivery rate targets.
- Close the gap between the idealized sorption materials that have been predicted and the synthesis of actual materials using low-cost source materials and synthesis processes such that cost target will be achieved.
- Cost: Typical high-surface-area, lightweight materials (e.g., activated carbon) are commercially manufactured in bulk at ~\$1/kg with carbon costs being only a small fraction. Thus, material costs for a system could be ~\$15/kg-H<sub>2</sub> (assume 7 wt%).
  - Develop sorbents using inexpensive materials and processes.
- Impact: NREL's H<sub>2</sub> storage material goals provide DOE with viable solutions that have the potential to meet even the ultimate technical targets. While this requires revolutionary materials, breakthrough technologies are being pursued.

### Objectives

NREL's research in the Hydrogen Sorption Center of Excellence (HSCoE) is targeted at addressing key technical barriers in DOE's Program for On-Board Hydrogen Storage:

- Weight and Volume: System capacities approach material capacities as the tank operation moves toward ambient temperatures and pressures with materials that have optimum binding energies. In general, sorbents already meet the vast majority of DOE hydrogen storage targets and have minimal heat transport requirements. NREL development efforts focus on the remaining targets, e.g., cost and capacity.
  - Volumetric and gravimetric capacities are closely linked in sorbents.
  - Increase material density (i.e., >0.7 g/ml) to decrease size.
  - Increase specific surface area and optimize pore sizes to decrease tank weight/size.
  - Optimize binding energies to increase capacities and operating temperature.
    - Develop the highest-efficiency storage system by optimizing sorbent materials that operate reversibly on-board with a

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage technical barriers section of the Fuel Cells Technologies Multi-Year Research, Development and Demonstration Plan:

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

This project is developing sorption materials for hydrogen storage systems. In general, the effort

focuses on creating hydrogen adsorption materials with optimized binding energy (10–25 kJ/mol) such that the system may operate at near-ambient temperatures and moderate pressures (Table 1). The design and synthesis of these hydrogen storage materials is aimed at meeting the following DOE hydrogen storage targets:

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

### Accomplishments

- Developed novel scalable synthetic processes (e.g., templating) to form high-surface-area, lightweight materials with optimum pore structure and composition for H<sub>2</sub> storage. These techniques accelerate development by increasing appropriate material synthesis rates where all the higher H<sub>2</sub> binding energy sites are accessible.
- Developed materials with ~15% B substitution in C and demonstrated that this increases capacity and binding energy. The enhanced binding energy is sufficient to store substantial hydrogen within the

DOE target temperature range of ~220 to 350 K; in good agreement with theoretical models.

- Theory and experiment continued to iteratively interact to design and synthesize several new H<sub>2</sub> storage materials. From the outset of the HSCoE, the ability to synthesize, stability, and DOE targets have been selection criteria for the design of new materials. Also, theory always works closely with experiment to find viable synthetic paths.
- Validated the initial theoretical prediction of single metal atoms dispersed and stably supported on a matrix being able to reversibly hold more than 2 H<sub>2</sub> [1]. This was done by demonstrating that the same models accurately predict the number of H<sub>2</sub> molecules adsorbed and the binding for the Ti-Silica system [2]. This removes all doubt to the validity of the predictions and indicates that we have routes to meeting DOE's ultimate storage targets.
- Identified new inexpensive materials that use the unique properties of Ca with very viable synthetic routes. These revolutionary new materials could store H<sub>2</sub> at >100 g/L and >10 wt%, exceeding all of DOE's ultimate targets including cost and volumetric/gravimetric capacities [3].

**TABLE 1.** Summary of Hydrogen Storage Properties for Materials Developed by NREL in Fiscal Year 2009

Storage Parameters/ Materials	Specific Energy (Net, wt%)	Volumetric Energy (Net, g/L)	Binding Energy (KJ/mol)	Conditions	Besides Cost, other targets of issue	Comments
DOE Targets	5.5	40	NA			
BC <sub>x</sub> (E)	1.4	1	11	77 K, 2 bar		Only 240 m <sup>2</sup> /g, 3x more than AC with same SSA
2.7 H <sub>2</sub> -Ti-Amor-silica (T)	NA	NA	31	2.4 H <sub>2</sub> /Ti		Agrees w/2.7 H <sub>2</sub> /Ti exper.
Li-BC <sub>8</sub> (E)	NA	NA	10-15	RT, 1 bar		10x gain over AC, 5 m <sup>2</sup> /g
CaC <sub>14</sub> (H <sub>2</sub> ) <sub>8</sub> (T)	>10	>100	20-40	RT		Proof of unique Ca properties
Ca-COF(H <sub>2</sub> ) <sub>4</sub> (T)	5.6	44		RT		Viable synthesis material
Hopping spillover kinetics (T)	NA	NA	~30	RT		1 <sup>st</sup> viable kinetic mechanisms
Hole assisted Kinetics (T)	NA	NA	~50	RT		1 <sup>st</sup> viable kinetic mechanisms
Ru, Pt, Pd-AC spillover (E)	1.2	6	20	RT, 80 bar	Catalyst, rate	Spillover on AC reproduced, 5x increase low P, higher rate
Li/THF co-int. Graphite (T)	5-7		5-20			
Li/THF co-int. Graphite (E)	0.5	NA		77 K 2 bar		Need to remove excess tetrahydrofuran
Li/THF co-int. Aerogel (E)	2.4	NA		77 K 2 bar		Down selected, not working
Ni(BF <sub>4</sub> ) <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> - SiO <sub>2</sub> aerogel (E)	~1	NA	20	77 K, 2 bar		Model system that showed coordinated Ni-H <sub>2</sub> binding. Down Selected, low capacity
Sc,Fe,Cr-organometalics (T)	4-8	20-40	15-25	ambient		
Sc,Fe,Cr organometalics (E)	NA	NA	NA	ambient		Down selected, little progress

NA – not applicable; E - experiment; T - theory; AC – activated carbon; SSA – specific surface area; RT – room temperature ; w/ - with

- NREL identified that barriers to migration are lowered sufficiently to enable spillover via structural and electronic features, and/or quantum mechanical tunneling where H will diffuse before it desorbs. These results provide development paths to create higher-capacity, higher-rate H storage spillover materials that can be used to meet DOE targets.
- NREL developed new catalyst processing that improved spillover capacity and charging rates. The decreased processing time, scalability, and improved performance will accelerate spillover materials' development to meet DOE targets.
- NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. An improved understanding of surface functionalization will enhance spillover.
- NREL improved measurement capabilities to provide more accurate and unique hydrogen storage materials characterization at high throughput.



## Introduction

NREL is leading the HSCoE to develop reversible sorbent materials for hydrogen storage within the U.S. DOE National Fuel Cell Technologies Program focused on vehicular and early market applications. The HSCoE is developing the science base and technology advances required to meet DOE storage goals by investigating a range of hydrogen sorbent materials. NREL performs research and development within the HSCoE on a variety of nanostructured and high-surface-area materials that may include carbon, metals, oxygen, and other lightweight elements. These materials show promise for breakthrough performance in hydrogen storage.

A guiding principle in developing the required material is that a continuum of energies exists for hydrogen bound to substrates and molecules. On the weak side of the continuum is non-dissociative physisorption due purely to van der Waals forces (4 kJ/mol). On the strong side is the full C-H chemical bond in methane with an energy of ~400 kJ/mol. Between these two limits, with binding energies between 10 and 50 kJ/mol, are the materials we are developing. The DOE goals can be met with sorption materials if (i) the energy for hydrogen adsorption can be designed to be in this optimal range, 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

To accelerate sorption materials' development, NREL is focused on four main areas:

- **Increase Matrix Binding Energy:** Increase concentration of substitution atoms (e.g., B for C) in lattices to adsorb dihydrogen directly (via donation), stabilize active species (e.g., transition metals) against agglomeration, and/or provide anchor points for building more complex sorbents.
  - 11 kJ/mol H<sub>2</sub> binding energy from B-substitution provides near-room-temperature sorption.
- **Increase Storage Site Access:** Develop stable high-surface-area, sub-microporous (<1 nm), light matrix materials that can either stabilize large quantities of hydrogen directly or provide frameworks for incorporating/stabilizing other components for hydrogen storage.
  - >2,500 m<sup>2</sup>/g SSA with 0.7 to 1.2 nm pore sizes may provide >6 wt% cryocompression.
- **Form Multiple H<sub>2</sub> Binding Sites:** To exceed DOE 2015 and meet DOE ultimate storage targets, fundamentally new approaches must be developed to store >7.5 wt% and >70 g/L hydrogen.
  - Requires >1 H<sub>2</sub> adsorbed at each binding site and material densities >1g/ml.
  - NREL is pioneering development of materials with multiple dihydrogen molecules per binding site.
  - Use inexpensive chemical and gas phase syntheses of organometallics.
  - Use viability in designs; theorists outpaced experiment.
  - Identify >10 wt% and >100 g/L dihydrogen storage materials.
- **Develop Near-Ambient Temperature Hydrogenation:** Develop detailed understanding using lightweight materials to reversibly store hydrogen via weak chemisorption processes. Investigate surface functionalization and catalyst integration to improve storage thermodynamics and kinetics.
  - NREL observed C-H bonds on reversible charge/discharge hydrogenation.
  - Improve processes and measurements to make stable reproducible materials.

By promoting accelerated progress in each of these areas and then deploying the knowledge obtained for the fabrication of optimized materials, systems that meet the DOE storage targets will be developed. NREL development efforts leverage each other and balance H<sub>2</sub> and material reactivity with the density and stability

of the sorption sites. NREL's vast amount of material design, selection, synthesis, and testing is only partially summarized in this report.

## Results

### Increasing Access to Higher-Binding Energy Sites:

In general, materials with high specific surface area can be created via pyrolysis processing of non-porous materials. However, materials made this way tend to have heterogeneous surface structures and a broad range of pore sizes, many of which are too large and thus have a substantial fraction of the hydrogen residing in the gas state rather than adsorbed onto surfaces. Creating optimized geometric structures in which all of the sorption sites are accessible to hydrogen requires the careful design of materials and the processes used. This issue is the same regardless of the sorption mechanism being employed, but does require that the structures be optimized for the desired type and conditions of the hydrogen storage. Templating is one technique being employed by NREL to enable systematic investigations of how specific structures and compositions affect hydrogen storage properties. Templating involves the vapor or chemical-phase deposition of a partial or full layer of material onto a porous structure. If, for example, carbon is coated onto a zeolite/template, the zeolite/template can be removed via chemical or vapor processing, leaving behind a porous carbon material that matches the geometric structure of the removed zeolite/template. This type of process has been used to make highly porous carbon materials (i.e., with specific surface areas over 3,500 m<sup>2</sup>/g) with pores that are nearly identical to the zeolite; resulting in materials with ~7 wt% hydrogen storage capacities [4]. NREL has used this technique to make novel lightweight hydrogen storage materials with optimized compositions and pore structures mimicking the template chosen. This technique accelerates development by increasing the synthesis rate of appropriate materials in which all the higher hydrogen binding sites are accessible.

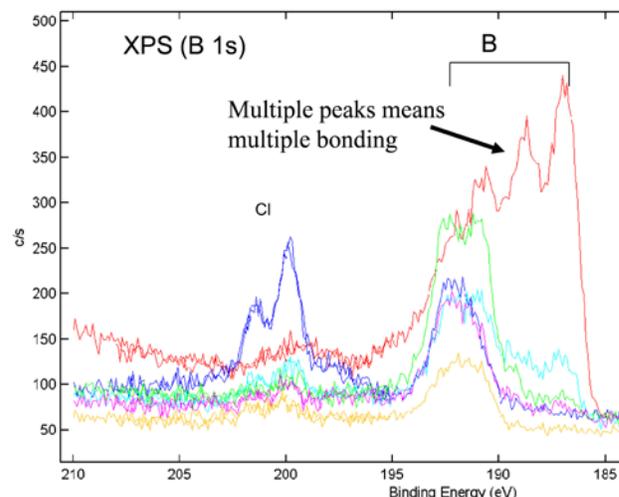
**Increasing Hydrogen Binding Energy with Substituted Elements:** NREL uses templating to make high-SSA materials, but more importantly, we have used this technique to make materials with higher binding energy sites. These higher binding sites are due to optimized pore sizes in the range of 0.4 to 1.2 nm, and/or they are associated with boron substitution in a carbon lattice (experimental demonstration of ~11 kJ/mol agrees well with calculations). Interest in the use of boron-substituted carbon nanomaterials has increased due to observed increases in hydrogen storage capacity through both computational and early experimental studies. This enhanced adsorption capacity will occur at all temperatures and thus enables improved near-ambient-temperature (i.e., ~220 to 350 K) hydrogen storage. Apart from using these

substituted nanostructures on their own, the boron (and possibly nitrogen-substituted carbon) sites also provide a means for partially coordinating and stabilizing metal atoms to create complexes that more strongly bind dihydrogen or enable multiple dihydrogens to be adsorbed at each metal site [5].

The main challenges for creating highly loaded boron substituted carbon include:

- As the boron composition increases, the specific surface area tends to decrease.
- The boron must be sp<sup>2</sup> coordinated in the carbon structure to enhance binding properties.

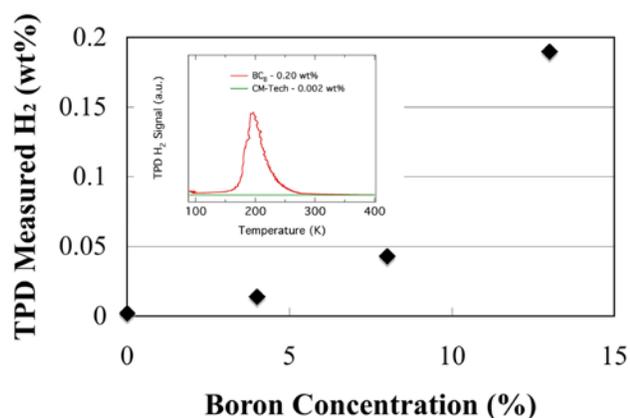
NREL is developing processes to form B-substituted C materials with high B composition and high SSA. For example, the use of vapor phase boron trichloride with benzene at ~1,100 K is a well-known process that forms BC<sub>x</sub> films [6]. NREL uses this and other processes to deposit BC<sub>x</sub> films on templates. By controlling the processing conditions and precursor materials, NREL produced materials with ~15% boron substituted in the carbon lattice. With X-ray photoelectron spectroscopy (XPS) data, we can quantitatively determine the amount of B and the binding environment (Figure 1). These XPS data indicate that the B in the BC<sub>x</sub> materials is typically in multiple binding states. However, by changing the processing conditions, we can increase the amount of B in the appropriate binding state that enhances adsorption. Through the use of temperature-programmed desorption (TPD) measurements, NREL also demonstrated that BC<sub>x</sub> materials store hydrogen more strongly than, for example, the template material being used, and that changes in processing affect the amount of B in the materials and the amount of hydrogen stored (Figure 2). As seen in Figure 2, as



**FIGURE 1.** XPS of BC<sub>x</sub> materials – the multiple B peaks indicate that the boron has multiple coordination states.

the boron composition in the  $BC_x$  films increases, the hydrogen measured by TPD increases and is typically ~100 times more than what is observed with the template materials alone, under the same conditions. NREL will continue improving the  $BC_x$  processing to create hydrogen storage materials with B compositions over 20% and specific surface areas over  $3.000 \text{ m}^2/\text{g}$ , and should demonstrate net hydrogen storage material capacities  $>5 \text{ wt}\%$ ,  $>50 \text{ g/L}$  at  $\sim 220 \text{ K}$ . NREL will use XPS, infrared spectroscopy, nuclear magnetic resonance, and neutron scattering to quantify the electronic and hydrogen storage properties of the  $BC_x$  materials to help guide and accelerate the improvement of the materials.

**Coordinated Metal Centers to Enhance Hydrogen Sorption:** NREL has championed the use of lightweight metals (i.e., first-row transition metals and group I and II elements) to enhance the binding of dihydrogen on matrix materials and, perhaps more importantly, the ability to create sorption sites that can store more than one dihydrogen molecule [1]. Since the publication of our seminal paper in this area, theorists and experimentalists have worked closely at NREL to iteratively design and synthesize new materials with coordinated metal centers. From the outset, we have strictly adhered to the criteria of synthesizing stable materials that have the potential to meet DOE hydrogen storage targets. Thus, theorists not only identify new materials, but work with experimentalists to identify thermodynamically viable synthetic paths to form stable materials. In addition, the calculations used to identify these novel materials have been validated with all known 3d metal- $H_2$  experimental results. Thus, there is good agreement for both the binding energy and the number of dihydrogens being stored between the theory and the known experimental results.



**FIGURE 2.** TPD (inset) measurements of templated  $BC_x$  materials made by NREL indicate that the hydrogen storage capacity at  $\sim 200 \text{ K}$  and vacuum pressure increases with increasing boron concentration. Since these results were performed under vacuum pressures, the data indicate that the hydrogen is more strongly bound by the  $BC_x$  materials than is typically observed with porous carbon materials.

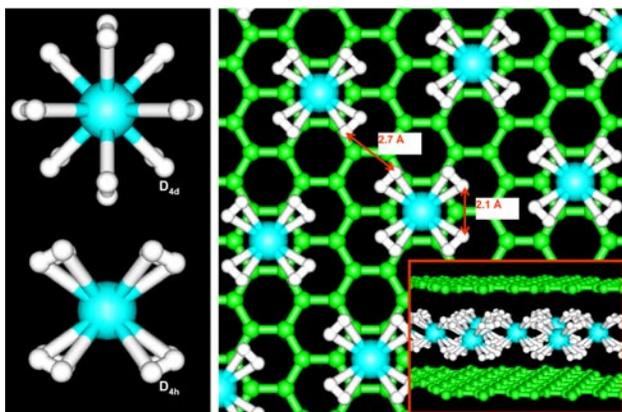
While single metal atom decoration of pure element matrices is possible without metal agglomeration, metal atoms are typically stabilized further at dopant sites (e.g., boron in carbon), and/or with H ligands. Thus, while several investigators have attempted to synthesize materials with single metal atoms coordinated on surfaces, most materials synthesized to date may only be marginally stable, and thus positive results have to date been limited. In addition, the reactivity of coordinated but electronically active metal sites indicates that great care must be taken to ensure that contamination and durability issues are adequately addressed. Recently, metal organic framework (MOF) materials with open Mn metal sites were fabricated with strong dihydrogen binding [7]. These results were in very good agreement with NREL's calculations [5] (experiment  $1 H_2$  at  $10 \text{ kJ/mol}$ ; theory  $1 H_2$  at  $8.4 \text{ kJ/mol}$ ), making this another example that confirms our models. However, the recent work by Hamaed et al. [2] is perhaps the most compelling confirmation to date. In this work, Ti dispersed on amorphous-silica internal surfaces are coordinated via strong Ti-silanol bonds (i.e.,  $\sim 400 \text{ kJ/mol}$ ). However, each Ti atom still has sufficient reactivity to adsorb multiple dihydrogen molecules. Once again, the experimental results ( $2.7 H_2$  at  $<22 \text{ kJ/mol}$ ) and models ( $2.4 H_2$  at  $<31 \text{ kJ/mol}$ ) are in good agreement. But more importantly, these experimental results confirm the basic premise of NREL's original work that an open metal site can store more than 2 dihydrogen molecules with energies appropriate for reversible hydrogen storage at ambient temperatures.

NREL worked with Lawrence Livermore National Laboratory (LLNL) over the previous year to form similar open Ni metal centers via  $Ni(BF_4)_2(PPh_2)_2 - SiO_2$  aerogels. In this work, we experimentally measured  $1 H_2/Ni$  at  $\sim 25 \text{ kJ/mol}$ , which again was in good agreement with theoretical estimates. (More information about the process is available in the LLNL section of this report, see IV.C.1j.) In this work, NREL and LLNL experimentalists and modelers worked closely to identify and systematically develop materials using well-established chemistries. Based on the successes of the Ni-silica aerogel and Ti-silanol work, we have fully validated the designed-material approach to forming strong dihydrogen adsorption with open metal centers. This work is applicable to most metals (e.g., Li, Na, Mg, Ca, Sc, Ti, V, Mn, Co) and matrix materials. However, NREL will apply our expertise to designing and synthesizing more stable and promising materials. For example, NREL has experimentally demonstrated that B substituted in carbon stabilizes open metal atoms to enable stronger dihydrogen binding. NREL demonstrated these principles with Li, Co, and Fe; all of these indicate that, in agreement with theory [1], the metal-matrix binding and the specific metal atom affect the number and binding energy of dihydrogen.

In the case of Li and possibly most solution-phase processes, boron substitution in carbon is required to stabilize the Li atoms and enable dihydrogen adsorption. With our unique promising results, NREL will pursue materials/process optimization to increase the number of viable binding sites and ultimately the overall storage capacities.

In this regard, NREL was the first to submit a paper that identified the special properties of inexpensive Ca. Here again, NREL applied our unique predictive  $M-xH_2$  theories to investigate the hydrogen storage properties of group I and II metals. Unlike Li, Na, and Mg, Ca can be coordinated to matrix materials in such a way that a pseudo 3d band state forms, enabling substantial amounts of dihydrogen to be reversibly adsorbed. For example, Ca-intercalated graphene (Figure 3) with the graphene layers separated sufficiently to allow dihydrogen molecules access around the Ca atoms, has the potential to have net hydrogen capacities in excess of 100 g/L and 10 wt%. In this case, the Ca atoms are stabilized by the carbon with a +1.3 charge transfer at 50–90 kJ/mol. Furthermore, the Ca atoms adsorb dihydrogen at 20–40 kJ/mol. The Ca-C binding and charge transfer are sufficiently strong to prevent Ca clustering; they become weaker as more dihydrogens adsorb. The Ca- $xH_2$  binding is sufficient to store and release dihydrogen at densities much higher than liquid hydrogen, but at ambient temperatures and moderately low pressures (i.e., 4 to 30 bar). Even though the synthetic pathways remain a challenge, this set of work provides a breakthrough that clearly defines sorbent materials that could be used to meet DOE's ultimate storage targets.

In addition to the initial Ca-graphene work, NREL also found that graphitic B-C and some covalent-organic framework (COF) and MOF materials stabilize open Ca centers. In the case of COFs (Figure 4), two Ca atoms

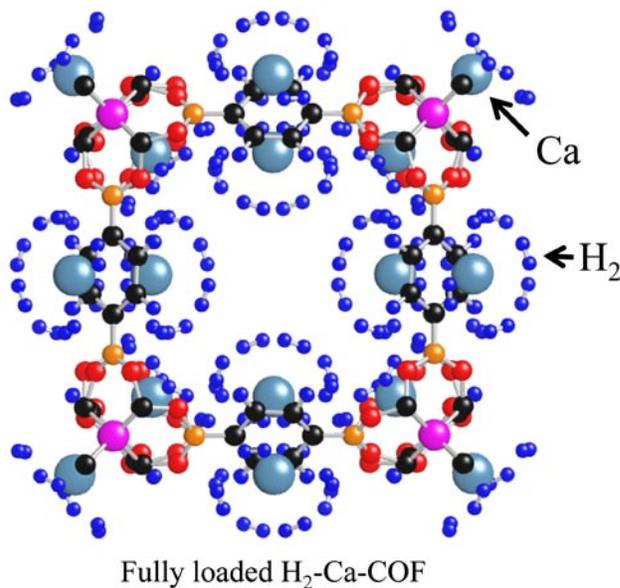


**FIGURE 3.** Novel calcium-intercalated graphene materials have exceptional hydrogen storage capacities over 100 g/L and 10 wt%. In this case, the Ca atoms are stabilized by the graphene at a +1.3 charge, which is sufficient to prevent agglomeration.

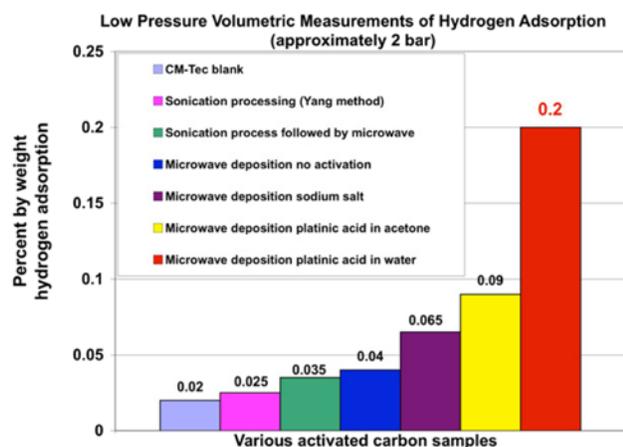
will be bound to the benzene linkers at ~120 kJ/mol, which in turn will adsorb four dihydrogen molecules with an average binding energy of 15 kJ/mol. Although this particular material will have a hydrogen storage capacity of only ~44 g/L and 5.6 wt%, the theorists and experimentalists have worked together to identify materials with very viable synthetic pathways.

**Weak Chemisorption of Hydrogen:** The HSCoE is developing spillover materials to provide ambient-temperature hydrogen storage. NREL's efforts to develop weak-chemisorption hydrogen storage materials include:

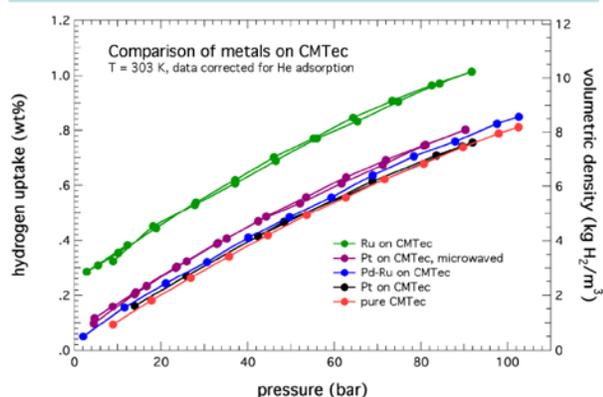
- **Improved spillover material processing** to reproducibly make materials with higher kinetics and hydrogen storage capacities. In general, improved catalyst processing increases hydrogen storage rates and capacities. Thus, NREL developed processes that drastically reduced the deposition times and uniformly deposited catalyst with particle sizes to >1 nm with several different metals (e.g., Pt, Pd, Ru) on different types of receptor materials (e.g., activated carbon,  $BC_x$ ). Initial results indicate that NREL's improved catalysts were stable for multiple cycles, and the low-pressure hydrogen uptake increased by a factor of five (Figure 5). The  $BC_x$  material also improved spillover material properties. In addition, the spillover binding energies for these materials were measured to be ~20 kJ/mol, and the higher-pressure loading improved to ~85% of maximum in ~5 minutes, which is a substantial



**FIGURE 4.** COF materials will stabilize two Ca atoms at each benzene linker to form a hydrogen storage material in which each Ca atom can reversibly adsorb 4 dihydrogen molecules to provide ~44 g/L and 5.6 wt% storage at ~15 kJ/mol. The Ca is bound to the COF benzene linker at ~120 kJ/mol, which does not collapse when the Ca is added.



#### High Pressure H Sorption on AC Materials have >1.0 wt%



**FIGURE 5.** Hydrogen spillover results indicate that improved catalyst processing enhances capacity (top). Irreproducibility in the processing often results in limited hydrogen spillover. However, with appropriate processing, hydrogen spillover (e.g., Ru on CMTEC data) is observed (bottom).

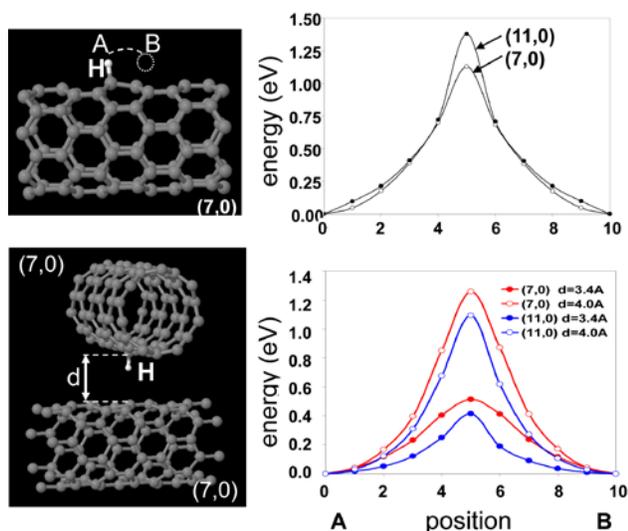
improvement from <60% for previous spillover materials. In general, NREL's catalyst deposition processing is scalable to large quantities, is applicable to inexpensive catalyst material (e.g., Ni), and may enable the use of substantially less catalyst. The decreased processing time, scalability, and improved performance will accelerate spillover materials' development while reducing costs to meet DOE targets.

- Surface Functionalization:** NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. In general, surface composition and properties of the receptor material are important for hydrogen diffusion. For example, reactions with oxygen surface moieties can inhibit or promote hydrogen spillover. TPD analysis of desorbed gases from spillover samples indicates that when some oxygen moieties are present, reduction processes occur to form water, CO<sub>2</sub>, CO, CH<sub>4</sub>, and other hydrocarbons. This indicates that

some functional groups interact with the absorbed hydrogen to create irreversible chemical reactions. This result explains some of the irreversibility and hysteresis observed in some data, and indicates the importance of monitoring the effluent from spillover measurements to ensure that the hydrogen storage capacity results are being accurately determined. From our work, because higher oxygen content in the receptor material resulted in higher secondary-reaction products such as water, we recommend that careful analysis be performed whenever oxygen is present in the spillover materials. NREL will continue to systematically perform research with model systems in conjunction with calculations and species-specific characterization, (e.g., TPD, Fourier transform infrared spectroscopy, Raman scattering, neutron scattering, and nuclear magnetic resonance [NMR]) to further define how surface species affect H spillover processes including enhancing diffusion and capacities.

- Discovery of H Diffusion Mechanisms:** NREL was the first to identify that barriers to migration are lowered sufficiently to enable spillover via structural and electronic features, and/or quantum mechanical tunneling where H will diffuse before it desorbs. While previous work at NREL and in the HSCoE established the thermodynamic principles for hydrogen dissociation and transport from the catalysts, and for atomic hydrogen storage on the receptor materials, the specific mechanisms for hydrogen diffusion on the receptor materials are not clearly understood. Based on calculations, NREL identified that H migration increases substantially via hopping between surfaces that are closely spaced (Figure 6). This suggests that perhaps layered or corner structures may enable hydrogen atom diffusion via hopping. Similarly, calculations indicated that free holes lower the barrier energy of H atom diffusion due to the H strong negative-potential behavior. In this case, the barrier drops for graphene from 1.04 eV H<sup>0</sup> to 0.60 eV for H<sup>+</sup> and for MOFs from 1.52 eV H<sup>0</sup> to 0.52 eV for H<sup>+</sup>. Thus, doping, defects, or functionalizations that form holes may enhance hydrogen storage via spillover. Finally, ambient-temperature quantum tunneling lowers the diffusion barrier energy. These results provide development paths to creating higher-capacity, higher-rate H-storage spillover materials that may be used to meet DOE system targets.

**NREL Collaborations and Partnerships:** As HSCoE lead and a leader in H<sub>2</sub> storage materials development and measurements, NREL collaborates with a large number of groups and institutions around the world. This includes working with the HSCoE partners, DOE Basic Energy Sciences projects, and independent projects, and participating directly with the HSECoE and the DOE Storage System Working



**FIGURE 6.** Initial calculations at NREL identified that, compared to migration along a surface, hopping between closely spaced surfaces substantially lowers the barrier for hydrogen diffusion.

Analysis Group. These interactions have led to several joint publications, and NREL has performed ~200 sample measurements this year to assist partners and collaborators in characterizing their hydrogen storage materials.

## Conclusions

- Experiments validate the original NREL predictions that single metal atoms dispersed and stably supported on a matrix can reversibly hold more than 2 H<sub>2</sub>. NREL was the first to use this theory to identify the unique properties of Ca.
- Experiment and theory worked together to identify new inexpensive Ca-based materials with viable synthetic routes to store H<sub>2</sub> at >100 g/L and >10 wt% at ambient temperatures. Since these materials will exceed liquid hydrogen densities at ambient temperatures, they may be used to meet DOE's ultimate targets including cost and capacities.
- Systematic experiments determined that improved surface/material processing increases spillover capacity and sorption rates. Some surface modifications including substitution, functional groups, and post-treatments affect the hydrogen storage capacities for spillover.
- Oxygen and other functional groups can react with spilled-over hydrogen to form irreversible and irreproducible chemical reactions that may adversely affect the reversible hydrogen storage capacity. Additional measurements need to be routinely performed to ensure that secondary reactions are not accounting for substantial amounts of the measured hydrogen storage capacities.

- NREL was the first to identify potential mechanisms that lower the barrier to hydrogen diffusion on receptor materials. Hopping between closely spaced surfaces, free-holes, and quantum-tunneling effects can all substantially increase hydrogen migration. These insights provide pathways for improving hydrogen spillover capacities and kinetics.
- NREL developed templating techniques to create high-specific-surface-area carbon and BC<sub>x</sub> materials.
- NREL developed B-substituted carbon materials with ~15% boron and relatively high specific surface areas. The B needs to be in sp<sup>2</sup> coordination to enhance dihydrogen binding. Thus, NREL needs to increase the B concentration, the amount of B in the correct state, and the specific surface areas of the materials.
- Open metal center coordination is stabilized at boron and nitrogen sites substituted in carbons. In addition, these materials enhance spillover capacities when a catalyst is deposited.

## Future Directions

### FY 2009

- Optimize templating processes to synthesize high-surface-area materials with >2,500 m<sup>2</sup>/g, <1 nm pore diameters, and/or boron concentrations >20%.
- Develop/improve gas-phase synthesis of targeted carbon and non-carbon sorbents.
- Create stable, coordinated, unsaturated metal centers with higher site densities that have substantial hydrogen storage using inexpensive materials including Li, Na, Ca, transition metals, and BC<sub>x</sub>.
- Use model systems and processing to construct specific surface features to test designs for improving spillover.
- Perform appropriate characterization (infrared, Raman, TPD, Neutron scattering, NMR) to determine the H state on the receptor.
- Accelerate theoretical efforts to design viable materials and synthetic routes.
- Continue to develop state-of-the-art measurement techniques and to provide high-throughput measurement for partners.
- Down-select materials and help with center go/no-go decisions based on material/system potentials.

### FY 2010

- Wrap up materials development and characterization and work with the hydrogen sorption community to recommend materials/routes for future development efforts.

- Scale up synthesis of most promising materials for round-robin verification of samples.
- Provide materials/systems recommendations for HSECoE.
- Determine viability of high-surface-area materials to meet DOE 2010, 2015, and ultimate targets.
- Quantify the enhancements produced by substitutions for dihydrogen binding and metal stabilization.
- Demonstrate the ability to form and quantify the H<sub>2</sub> binding of metal centers and their ultimate storage potential.
- Quantify the potential of weak chemisorption along with the effects of intrinsic and functionalized material properties.

### Special Recognitions and Awards/Patents Issued

1. “Metal-doped single-walled carbon nanotubes and production thereof,” A.C. Dillon, M.J. Heben, T. Gennett, P.A. Parilla, PCT Patent WO03/085178.
2. Hydrogen Electrochemical Energy Storage Device, L.J. Simpson, Patent submitted USPTO (2008).
3. “Continuous Growth Of Single-wall Carbon Nanotubes Using Chemical Vapor Deposition,” (Inventors: Grigorian; Leonid; Hornyak, Louis; Dillon, Anne C.; Heben, Michael J., Patent 7,431,965.

### FY 2009 Publications

1. “Ab initio calculations predicting the existence of an oxidized calcium dihydrogen complex to store molecular hydrogen in densities up to 100 g/L,” Y.-H. Kim, Y.Y. Sun, and S.B. Zhang, *Phys. Rev. B* **79**, 115424 (2009).
2. “Ab initio Design of Ca-Decorated Organic Frameworks for High Capacity Molecular Hydrogen Storage with Enhanced Binding,” Y.Y. Sun, Kyuho Lee, Yong-Hyun Kim, and S.B. Zhang, *Appl. Phys. Lett.*, accepted (2009).
3. “Computational studies on hydrogen storage in aluminum nitride nanowires/tubes,” Yafei Li, Zhen Zhou, Panwen Shen, S.B. Zhang, and Zhongfang Chen, *Nanotechnology* **20**, 215701 (2009).
4. “Ti-Substituted Boranes as Hydrogen Storage Materials: A Computational Quest for the Ideal Combination of Stable Electronic Structure and Optimal Hydrogen Uptake,” Cheng-Gen Zhang, Renwu Zhang, Zhi-Xiang Wang, Zhen Zhou, Shengbai B. Zhang, and Zhongfang Chen, *Chem. Eur. J.* **15**, 5910–5919 (2009).
5. “Opening Space for H<sub>2</sub> Storage: Cointercalation of Graphite with Metal and Small Organic Molecules,” Yufeng Zhao, Y.-H. Kim, L.J. Simpson, A.C. Dillon, S.-H. Wei, and M.J. Heben, *Phys. Rev. B*, **78**, 144102 (2008).

6. “Boron-Based Organometallic Nanostructure: hydrogen-storage properties and structure stability,” Y. Zhao, M.T. Lusk, A.C. Dillon, M.J. Heben, and S.B. Zhang, *Nanoletters* **9**, 157–161 (2008).
7. “An in situ electrical study on primary hydrogen spillover from nanocatalysts to amorphous carbon support,” C.K. Lin, Z.Z. Yang, T. Xu, and Y.Z. Zhao, *Appl. Phys. Lett.* **93**, 233110 (2008).
8. “Mechanism of Hydrogen Storage on Reduced Carbon Single-Walled Nanotubes,” Calvin J. Curtis, Thomas Gennett, Chaiwat Engtrakul, Kevin O’Neill, Jamie E. Ellis, and Michael J. Heben, *Fall MRS Proceedings* (2008).
9. “Nanoengineered Carbon Scaffolds for Hydrogen Storage,” Ashley D. Leonard, Jared L. Hudson, Hua Fan, Richard Booker, L. J. Simpson, K. J. O’Neill, P. A. Parilla, Michael J. Heben, Carter Kittrell, Matteo Pasquali, and James M. Tour, *Journal of the American Chemical Society* (2008).
10. “Challenges of a Hydrogen Economy: A Novel Organometallic Fe-C60 Complex for Vehicular Hydrogen Storage,” E. Whitney, C. Engtrakul, C.J. Curtis, K.J. O’Neill, P.A. Parilla, L.J. Simpson, Y. Zhao, Y.-H. Kim, S.B. Zhang, M.J. Heben, and A.C. Dillon, *Mat. Res. Soc. Proc. Spring Meeting* (2008).
11. “Rich Chemistry and Structure Rule of sp<sup>2</sup> and sp<sup>3</sup> Boron,” Y. Zhao and A.C. Dillon, submitted.
12. “Spin crossover induced by molecular hydrogen adsorption in Fe(II)-exposed metal organic frameworks,” Y.Y. Sun, Y-H Kim, K. Lee, D. West, and S.B. Zhang, *J. Am. Chem. Soc.*, under review (2009).
13. “Symmetry-assisted hydrogen adsorption and control on transition metal incorporated porphyrins,” Y-HyKim, Y.Y. Sun, W.I. Choi, J. Kang, and S.B. Zhang, *Phys. Rev. Lett.*, under review (2009).
14. “Structural stability and hydrogen storage properties of Ti anchored on silica,” Lee, K.; Lucking, M.; Sun, Y.Y.; Chen, Z.; Zhang, S., (to be submitted to *Nano Lett.*).
15. “Energetics of hydrogenation of single-walled carbon nanotubes,” Y. Zhao et al, in preparation.
16. “Hydrogenation Mechanism for the Reaction of Single-Walled Carbon Nanotubes with Tetrahydrofuran,” T. Gennett, C. Engtrakul, C. Curtis, J.E. Ellis, J. Blackburn, A.C. Dillon, L. Simpson, K. Jones, P. Parilla, and M. Heben. Submitted to *J. Am. Chem. Soc.*
17. “Self-Mediated Hydrogen Migration in Pure Carbon Materials,” C.V. Ciobanu and Yufeng Zhao, in preparation.
18. “Effect of Surface Area and Microporosity of Microporous Carbon Materials Prepared from Decomposition of PEEK Polymer on the Hydrogen Storage Capacity and Binding Energy,” Thomas P. McNicholas, Simiao Zhang, Yanqin Wang, Lin Simpson, Alfred Kleinhammes, Yue Wu, and Jie Liu. In Preparation (2008).
19. “Hole mediated diffusion of H on sp<sup>2</sup> carbon networks,” D. West, K. Lee, and S.B. Zhang, to be submitted to *Phys. Rev. Lett.*

20. Woon Ih Choi, Seung-Hoon Jhi, Kwiseon Kim, and Yong-Hyun Kim, "Divacancy-nitrogen-assisted transition metal dispersion and hydrogen adsorption in defective graphenes: A first-principles study," to be submitted to *Phys. Rev. Lett.* (2009).

### FY 2009 Presentations

1. DOE HSCoE Overview, [A.C. Dillon](#) (invited talk) DOE Annual Merit Review, May 18-21, 2009.
2. Hydrogen Sorbent Development within the HSCoE, [L.J. Simpson](#) (invited talk), DOE Annual Merit Review, May 18-21, 2009.
3. Novel H<sub>2</sub> storage approaches using organometallics, [Shengbai Zhang](#), (invited talk) APS March Meeting, Pitt., PA, Mar. 19, 2009.
4. First-principles study of dihydrogen interaction of porphyrin-like nitrogen-doped graphenes, [Woon Ih Choi](#), Seung-Hoon Jhi, Kwiseon Kim, and Yong-Hyun Kim, APS March Meeting, Mar. 19, 2009.
5. Nanostructured Adsorbents for Hydrogen Storage, [L.J. Simpson](#), K. O'Neill, P.A. Parilla, C. Engtrakul, T.G. Gennett, J.L. Blackburn, Y. Zhao, A.C. Dillon, E. Whitney, C. Curtis, and M.J. Heben, APS March Meeting, Pittsburgh, PA, Mar. 19, 2009.
6. Energy storage in nanostructured materials, [Y-H Kim](#), (invited talk) APS March meeting, Mar. 16, 2009.
7. Overview of the DOE Hydrogen Sorption Center of Excellence, [A.C. Dillon](#), (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
8. Theory Activities in HSCoE, [Y. Zhao](#), (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
9. Cluster 4: Spillover (Weak Chemisorption), [T.G. Gennett](#), (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
10. Strong Binding of H<sub>2</sub> (RC3) Technical Update, [Chaiwat Engtrakul](#), (invited talk) DOE Tech Team Review, Detroit, MI, Jan. 15, 2009.
11. Mechanism of Hydrogen Storage on Reduced Carbon Single-Walled Nanotubes, Calvin J. Curtis, Thomas Gennett, Chaiwat Engtrakul, Kevin O'Neill, Jamie E. Ellis. and Michael J. Heben, Fall MRS proceedings 2008.

12. Nanostructured Adsorbents for Hydrogen Storage, [L.J. Simpson](#), K. O'Neill, P.A. Parilla, C. Engtrakul, T.G. Gennett, J.L. Blackburn, Y. Zhao, A.C. Dillon, E. Whitney, C. Curtis, and M.J. Heben, NanoEnergy Conference, Paris, France, 10/20/08.

13. Hydrogen Storage Materials, [L.J. Simpson](#), K. O'Neill, P.A. Parilla, C. Engtrakul, T.G. Gennett, J.L. Blackburn, Y. Zhao, A.C. Dillon, E. Whitney, C. Curtis, and M.J. Heben, (Invited Colloquium) University of Trento, Trento, Italy, 10/27/2008.

14. Simulating real materials for our energy future, [Shengbai Zhang](#), High Performance Computing Conference, Troy, NY 10/22/08.

15. Simulating our energy future, [Shengbai Zhang](#), (Department of Physics Colloquium), SUNY at Buffalo, Buffalo, NY 10/16/08.

16. Theory for Hydrogen Storage in Organometallic Nanostructures, [Y. Zhao](#), (invited Colloquium), Department of Chemistry and Biochemistry, Northern Illinois University, Sept. 22 (2008).

### References

1. Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, S.B. Zhang, *Phys. Rev. Lett.* **2005**, *94*, 155504.
2. Hamaed et al., *JACS* **2008**, *130* 6992.
3. Y-H Kim, et al., *PRB* **2009**, *79*, 115424. submitted in 2007.
4. e.g., Yang et al., *JACS* **2007**, *129*, 1673. Wang et. al., *J. Phys. Chem. C* **2008**, *112*, 12486.
5. Y-H Kim et al., *PRL* **2006**, *96*, 16102, also see Yakobson's 2009 DOE Annual Merit Review Presentation.
6. e.g. Kouvetakis, *J. Chem. Soc. Chem. Comm.* **1986**, 1758.
7. M. Dinca, et al., *JACS* **2006**, *128*, 16876.