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

Objectives

NREL’s research in the Hydrogen Sorption Center of Excellence (HSCoE) is targeted at addressing key technical barriers in DOE’s sub-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 storage system 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 hydrogen binding energy in the range of 10–50 kJ/mol (for room temperature operation).
- Decrease heat-transfer requirements to increase on-vehicle 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.
- Develop sorbents using inexpensive materials and processes.

Impact: NREL’s H₂ 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.

Technical Barriers

This project addressed 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 sorbents for hydrogen storage systems. In general, the effort focuses on creating hydrogen adsorption materials with optimized binding energy (10–30 kJ/mol) such that the system may operate at near-ambient temperatures and moderate pressures. 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 optimal pore structure and composition for H₂ storage.
- Developed materials with ~5% sp² coordinated boron substitution in carbon (BCₓ) and demonstrated that this increases capacity and binding energy. Also developed nitrogen (N) substituted in C and demonstrated that BCₓ improves spillover processes.
- Theory and experiment continued to iteratively interact to design and synthesize several new H₂ 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.
- Identified new inexpensive hydrogen sorbents with viable synthetic routes. These included materials like titanium (Ti)-graphite oxide that was experimentally synthesized and demonstrated enhanced dihydrogen adsorption.
- Identified that some oxygen groups are needed for spillover. Spillover does not occur when oxygen groups are missing, spillover rates and capacities are substantially increased when the correct oxygen groups are present, and secondary reactions with the H occur when other oxygen groups are present. These results provide development paths to create higher-capacity, higher-rate H storage spillover materials that meet DOE targets.
- Developed new catalyst processing that improved spillover capacity and charging rates. The decreased processing time, scalability, and improved performance helps spillover materials’ development.
- Worked with groups around the world to improve measurement capabilities to provide more accurate and unique hydrogen storage materials characterization at high throughput. This included helping to improve measurement calibrations at other laboratories that have clear issues with irreproducibility and data that are not consistent with standard sorption materials.
- Held workshops and Center partner meetings to develop a comprehensive set of accomplishments and recommendations for the HSCoE. In addition, NREL organized numerous conferences/conference sessions on hydrogen storage to ensure optimal dissemination of results that helps accelerate sorbent development.

Introduction

NREL led the HSCoE to develop reversible sorbent materials for hydrogen storage within the U.S. DOE National Fuel Cell Technologies Project focused on vehicular applications. The HSCoE developed the science base and technology advances required to meet DOE storage goals by investigating a range of hydrogen sorbents. NREL performed 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 of interest for sorbents. The DOE goals can be met with sorbents 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 development of sorption materials, we 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. Provides 11 kJ/mol H₂ binding energy from B-substitution to enable 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. Greater than 2,500 m²/g specific surface area (SSA) with 0.7 to 1.2 nm pore sizes may provide >6 wt% cryocompression.

- **Form Multiple H₂ 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 H₂ adsorbed at each binding site and material densities >1g/ml.
  - Develop materials with multiple dihydrogen molecules per binding site.
  - Use inexpensive chemical and gas phase syntheses of organometallics.
  - Combine theory and experiment to optimize development effort.
  - Identify new dihydrogen storage materials based on slight modifications to existing materials.

- **Develop Near-Ambient T 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. Improve processes and measurements to make stable reproducible materials.

**Results**

**Increasing Hydrogen Binding Energy with Substituted Elements:** We used templating to make high-SSA materials, but more importantly, we used this technique to make boron substituted carbon materials with higher binding energy sites (experimental demonstration of ~11 kJ/mol agrees well with calculations). 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 [1].

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

- As the boron composition increases, the SSA tends to decrease.
- The boron must be sp2 coordinated in the carbon structure to enhance binding properties.

NREL developed processes to form B-substituted C materials with high B composition and high specific surface area. For example, the use of vapor phase boron trichloride with benzene at ~1,100 K is a well-known process that forms BCₓ films [2]. 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 quantitatively determined the amount of B and the binding environment (Figure 1). These XPS data indicate that the B in the BCₓ materials is typically in multiple binding states. However, by changing the processing conditions, we can increase the amount

![Figure 1](image_url)

**FIGURE 1.** (a) High resolution B 1s spectrum and associated boron binding energies deposited BCₓ material. (b) C 1s spectra of the base material with and without BCₓ material deposited using different precursors.
of B in the appropriate binding state that enhances adsorption. The boron 1s and carbon 1s spectra are useful in determining the exact state of boron binding. Figure 1a shows the high-resolution B1s spectrum and the associated boron binding energies. The four main peaks are attributable to boron carbide, elemental boron, sp2 boron, and boron oxide. Based on the entire four binding energy peaks, a total atomic B composition value was determined to be 12.6% in this sample. The sp2 coordinated boron was ~4.5%. Another indication of the incorporation of boron into the graphitic carbon lattice is in the carbon 1s spectrum shown in Figure 1b. In this spectrum the base carbon peak is shifted from 284.5 eV, the recognized value for graphitic carbon, to 283 eV with an associated shoulder at 282 eV. The shift to lower binding energies and the shoulder in the spectrum is attributed to the boron-carbon binding sites.

Through the use of temperature-programmed desorption (TPD) measurements, NREL also demonstrated that BCx 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. The effects of enhanced hydrogen binding and perhaps smaller pore structures associated with BCx materials is also observed with TPD (Figure 2). In general, as the B content of the BCx materials is increased, the hydrogen takes a much longer time to desorb under vacuum conditions. This is consistent with a higher binding energy and/or a more tortuous path associated with the potential formation of smaller porous structures. That said, similar effects are not observed with nitrogen substituted templated carbon materials, suggesting that the higher binding energies associated with boron substitution is playing a major roll.

**Coordinated Metal Centers to Enhance Hydrogen Sorption:** NREL investigated 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 [3]. Theorists and experimentalists worked closely at NREL to iteratively design and synthesize new materials with coordinated metal centers. We 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. The calculations used to identify these novel materials were validated with all known 3d metal-H2 experimental results. There is good agreement for both the binding energy and the number of dihydrogens being stored between the theory and the known experimental results.

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. A specific example of this issue was demonstrated by NREL investigating Li integration with carbon materials. While all attempts to date have not observed enhanced hydrogen interaction effects using Li integrated with pure carbon supports, substantial interactions were observed when Li was integrated with BCx materials. This is in good agreement with theoretical calculations [3]. We used a boron-substituted carbon (BCx) and successfully lithiated it in a tetrahydrofuran solution of Li naphthalide. As shown in Figure 3, TPD measurements demonstrate the reversible desorption of hydrogen at <50°C following room temperature hydrogen exposure. Hydrogen desorption temperatures increased from -120°C to ~50°C by the addition of Li. These TPD measurements are consistent with NREL theoretical predictions that boron sites appear to provide well-defined Li metal binding sites. In addition, high-pressure hydrogen adsorption measurements on the lithiated BCx material at 100 bar and 30°C were ~1.5 times greater than the parent BCx material. Interestingly, the Brunauer-Emmett-Teller SSA of the Li-BCx material was only ~5 m²/g. Surprisingly, the H2 adsorption sites in the lithiated BCx were stable in O2 and H2O.

**Work by Hamaed et al. [4] demonstrated that Ti dispersed on amorphous-silica internal surfaces are coordinated via strong Ti-silanol bonds (i.e., ~400 kJ/mol). However, each Ti atom still has sufficient reactivity to adsorb multiple dihydrogen**
molecules. Once again, the experimental results (2.7 H₂ at <22 kJ/mol) and models (2.4 H₂ at <31 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 two dihydrogen molecules with energies appropriate for reversible hydrogen storage at ambient temperatures. In a similar approach, we identified that graphene oxide (GO) can be a potential substrate to covalently anchor transition metal atoms that are undercoordinated and well-exposed to accommodate multiple H₂ [5]. Zhang et al. reported that Ti atoms grafted on GO could bind multiple H₂ ligands with the desired binding energies (Figure 4, 14-41 kJ/mol-H₂). The gravimetric and volumetric densities for this system are predicted to be 4.9 wt% and 64 g/L, respectively. NREL developed a successful reaction pathway to synthesize Ti-GO by employing the theoretical calculations [5] to guide experimental investigations. The Ti-GO materials were isolated in an inert atmosphere and then exposed to 500 Torr of H₂. TPD measurements demonstrated enhanced H₂ binding sites with one benzyl fragment removed. Additional work is being performed to remove the other benzyl fragment to enable multiple dihydrogen adsorption.

**Weak Chemisorption of Hydrogen:** The HSCoE developed spillover materials with the potential for ambient-temperature hydrogen storage. We improved material processing, demonstrating enhanced spillover performance with boron substituted materials, and identified specific surface functional groups that affect spillover.

Improved spillover material processing: The objective was to reproducibly make materials with higher kinetics and hydrogen storage capacities. In general, improved catalyst processing increases hydrogen storage rates and capacities. Thus, we developed processes that reproducibly integrated catalysts (e.g., Pt, Pd, Ru) with controlled particle size (e.g. 1 to 2 nm) and structure, uniformly with different types of receptor materials (e.g., activated carbon, BC).

**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, CO₂, CO, CH₄, 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 content of some oxygen species in the receptor material results in higher secondary-reaction products such as water, we recommend that careful analysis be performed whenever oxygen is present in the spillover materials. That said, NREL performed experiments using carbon black (a well known commercial product with no oxygen species on the surface) with Ru catalysts and observed no substantial increase in hydrogen uptake. This suggests that the complete absence of oxygen functional groups prevents spillover. In addition, we synthesized Pt/ carbon from pyrolyzed sucrose templated on silica.
sphere templates, which contains substantial oxygen containing functional groups. This is partly due to the fact that to remove the silica template, the powder after pyrolysis was soaked in 6 M potassium hydroxide solution for four days, filtered, washed with deionized water and dried in at 120°C. The resultant material is highly functionalized. As shown in Figure 5, an enhancement of well over 30% is observed from the base material, and on a per specific surface area basis, the material has well over a 100% enhancement. All these results demonstrate that appropriately functionalized receptor materials can dramatically enhance hydrogen storage capacities at ambient temperature. In general, these materials have excellent kinetics (<5 min to saturation), are the first Pt catalyst based carbon substrate with spillover enhancement of hydrogen adsorption that has been observed at NREL, the adsorption of hydrogen was still increasing approximately linearly at 150 bar, and had minimal irreversibility (multiple cycles were conducted with no loss of sorption capacity or water/methane formation).

Calculations predict that the use of boron-substituted materials may enhance spillover. At the very least, boron substitution may help stabilize catalyst particles for use in weak chemisorption hydrogen storage. While SSA and boron concentration issues must be resolved for boron-substituted carbons, initial evaluations indicate that BCx materials with Ru catalyst provide highly reproducible and reversible spillover that is 20 to 30% above the base material (Figure 6). In general, the capacities of even the non-Ru containing materials are substantially higher on a per specific surface area (i.e. 750 m²/g) bases compared to activated carbons. The higher capacity observed with Ru catalysts while modest is well above detection limits, and unlike other materials used for spillover, this Ru/BCx material is extremely durable providing identical repeated performance even after multiple air exposures. The BCx material substantially enhances kinetics. The spillover binding energies for these materials were measured to be ~20 kJ/mol, and the higher-pressure loading improved to ~83% of maximum in ~5 minutes, which is a substantial improvement from <60% for spillover on pure carbon materials.

Overall, NREL demonstrated that substantial increases in hydrogen storage capacity can be achieved at ambient temperatures with weak chemisorption processes like spillover. While a significant amount of work is still required to develop highly reproducible and robust materials that have the high capacities demonstrated by the HSCoe with less durable materials, the clear indication is that weak chemisorption is a viable path for on-vehicle refuelable hydrogen storage.

**NREL Collaborations and Partnerships:** As the HSCoE lead and a leader in H₂ 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 HSCoE and the DOE Storage System Working Analysis Group. These interactions have led to
several joint publications, and NREL performed ~200 sample measurements this year to assist partners and collaborators in characterizing their hydrogen storage materials.

Conclusions

- Developed novel scalable synthetic processes using templating techniques to form high surface area lightweight materials with optimal pore structure and composition for H\textsubscript{2} storage.
- Demonstrated that B substitution in C increases capacity and binding energy when in the correct sp\textsuperscript{2} coordination. 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. NREL demonstrated that only a small amount of B in most of the BC\textsubscript{x} materials is in the correct coordination state with carbon.
- Identified and synthesized coordinated metal center materials for improved ambient storage of hydrogen. Materials with binding energies between 15 and 25 kJ/mol and/or multiple dihydrogen adsorption have been demonstrated. Ultimately, it should be possible to use these sorbents to meet DOE ultimate storage targets.
- Identified processes and surface functionalizations that helped to synthesize more robust, reproducible spillover materials. Improvements in catalysts and receptors including boron substitution and appropriate oxygen species led to enhanced hydrogen storage performance via weak chemisorption (spillover).
- Improved measurement capabilities and worked with Center partners and other groups around the world to provide more accurate H\textsubscript{2} storage materials characterization at high throughput. This included working with DOE to assemble and publish the best practices document on how to perform and interpret hydrogen storage measurements correctly.

Future Direction

- Establish relationships to improve hydrogen storage measurements techniques.
- Establish hydrogen sorbents working group for continued materials development independent of the HSCoE.

Special Recognitions and Awards/Patents Issued


3. Lin Simpson, HSCoE October 2009 HSCoE Face-to-Face Meeting and January 2010 Tech Team Meetings at College Station, TX.


FY 2010 Publications


12. Rich Chemistry and Structure Rule of sp\textsuperscript{2} and sp\textsuperscript{3} Boron, Y. Zhao, A.C. Dillon, submitted.


FY 2010 Presentations


References