NATIONAL RENEWABLE ENERGY LABORATORY

Innovation for Our Energy Future

2010 DOE Hydrogen Program Review NREL Research as Part of the Hydrogen Sorption Center of Excellence

2010 Annual Merit Review

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Project ID # ST021

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***Rensselaer Polytechnic Institute**

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Overview

Timeline

Center of Excellence start date: FY05

Center of Excellence end date: FY10

Percent complete: 95%

Barriers

General: A. Cost, B. Weight and Volume, C. Efficiency, E. Refueling Time

Reversible Solid-State Material: M. Hydrogen Capacity and Reversibility, N. Understanding of Hydrogen Physi- and Chemisorption, O. Test Protocols and Evaluation Facilities.

Budget

- $3.1 M in FY09
- $1.9 M in FY10

Partners

Rice (J. Tour), Rice (B. Yakobson, R. Hauge), Air Products (A. Cooper), Duke (J. Liu), CalTech (C. Ahn), LLNL (T. Baumann), NIST (D. Neumann, Craig Brown), ORNL (D. Geohegan), Penn State (V. Crespi), U. Michigan (R. Yang), University of Missouri (P. Pfeifer), University of North Carolina (Y. Wu), Texas A&M (J. Zhou), ANL (D.J. Liu). U. Chicago (L. Yu) + others outside of the COE

Relevance: Objectives

NREL's research in the HSCoE is focused on key technical barriers (A, B, C, E, M, N, O; slide 2) in DOE's Hydrogen Program for On-Board Storage: 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 Materials Development Focused on Capacity, Cost and Kinetics targets

1. **Volumetric and gravimetric capacities**
   - closely linked in sorbents
     - Increase material density (i.e., >0.7 g/mL) to maximize.
2. **Optimize accessible specific surface area and pore size** (decrease tank weight and size)
   - Scaffold materials
   - Templated materials
   - Next generation catalyst promoted "Weak" Chemisorption (spillover)
   - "Bridged" framework (MOFs) materials
3. **Tune binding energies to increase capacities and control operating temperature**
   - Substitutional materials
     - Boron, nitrogen integrated into matrix
   - Decrease heat transfer requirements to increase on-board refueling times
     - Sorption materials typically meet DOE refueling and delivery rate targets
4. **Improve kinetics for weak chemisorption, rate of hydrogen adsorption**
   - Optimize as pursuing 1-3.

Cost: Develop next-gen sorption materials using inexpensive materials and processes
Typical high surface area light weight materials (e.g., activated carbon) are commercially manufactured in bulk at ~$1/Kg with carbon costs only being a small fraction. Thus, material costs for a system could be ~$15/Kg-$H_2$ (assume 7 wt%).

Impact: NREL's H_2 storage material goals provides DOE with viable solutions and significant insights into how to meet to **the DOE 2015 and ultimate technical storage targets**.

Final Report. Final Deliverable that summarizes the success of past 5 year effort addresses key barriers overcome and remaining.

Technical Approach: Focused Materials Development

Control Hydrogen Binding Energy:

- Incorporate substitutional atoms (e.g. B and N) in carbon matrix to control the electronic, physiochemical structure/properties of substrate surface.
  - adsorb dihydrogen directly (via donation),
  - stabilize active catalyst species against agglomeration,
  - provide anchor points for building more complex sorbents.

* 11 kJ/mol H_2 binding energy from B-substitution provides near room temperature sorption

Control Storage Pore Structure : Develop stable high surface area, distinct pore diameter distribution, matrix materials that can either stabilize large quantities of hydrogen directly or provide frameworks for incorporating/stabilizing other components to enhance hydrogen sorption.

• Templated Materials Development: Zeolite/Silca templates with controlled pore distribution and surface area.

Form Multiple H_2 and H Binding Sites: To meet DOE ultimate storage targets, fundamentally new approaches must be developed to store >7.5 wt% and >70 g/L hydrogen.

Require ≈1 H per C at each binding site and material densities >1g/ml.

NREL pioneering development of materials with multiple dihydrogen molecules per binding site

•Use inexpensive chemical and gas phase syntheses of organometallic materials and MOFs

•NREL predicts >10 wt% and >100g/L dihydrogen storage materials @ 77K, 100bar.

Develop Near Ambient Temperature Hydrogenation: Develop detailed understanding using materials to reversibly store hydrogen via weak chemisorption (spillover) processes. Investigate surface functionalization, pore distribution and catalyst integration to improve storage thermodynamics and kinetics.

- NREL observed capacity enhancement on B-substituted and Silica Templated carbon materials.
- NREL showed multiple reversible charge/discharge hydrogenation processes with no capacity loss, i.e. no side reactions.
- Established protocols for improved processing and measurements on these stable reproducible materials

NREL development efforts are integrated across tasks and balance material reactivity with the density and stability of the H_2 sorption sites. Considerable focused effort on "spillover" materials in FY10. NREL's extensive efforts in material design, selection, synthesis, and testing is only partially summarized here.

Approach: Key FY 2010 Milestones/Deliverables

- Draft extended outline for HSCoE final report. Completed January 2010
- 1st complete draft of HSCoE final report in June 2010 time frame
- HSCoE Final Report submitted to DOE after review and revisions by September 2010
- Complete Sorption Publications e.g.
  - LixBCy compound or equivalent work, (manuscript under internal review May 2010.)
  - HSCoE joint publication
- Report on three new spillover materials completed March 2010
- Synthesize gram quantities of near ambient temperatures hydrogen adsorption materials and send materials to partners (e.g. NIST, UNC, SWRI®) for evaluation.

Approach: Integration

NREL Leads DOE Hydrogen Sorption Center of Excellence

- **Ensures all projects are highly integrated with other research within and outside the center**
  - Organizes numerous HSCoE meetings at the group & center level to ensure optimum coordination
  - Publishes a newsletter that provides partners with important information and new results
  - Coordinates partner input for DOE Annual Merit Review, Tech Team Review, and Annual Report
  - NREL helps coordinate materials down-selection, roadmap development, and re-direction efforts
  - Work on Sorption Center Go/No-Go decision process
  - Part of DOE Hydrogen Storage Engineering CoE providing material properties
  - Works with SSWAG for storage tank analysis
  - Provide input to DOE's EERE Risk Analysis Assessment for Storage
  - Provide technical information for management briefings and coordination efforts
  - Developed sorption measurement protocols to develop reporting consistency in/out of center

NREL provides the hydrogen storage community with leadership and technical development

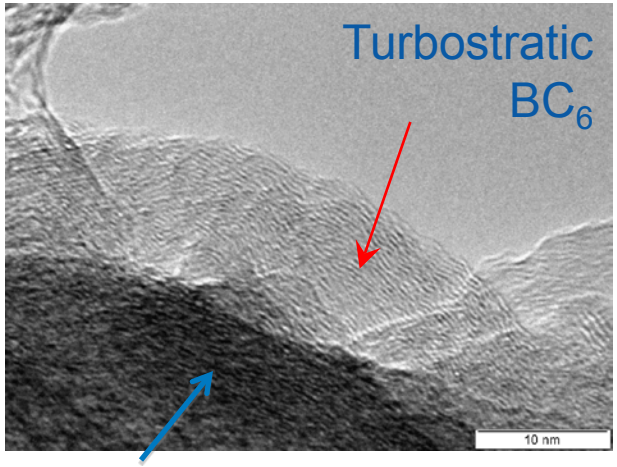
- Helps organize technical sessions at conferences around the world
  - 239th ACS National Meeting, "Chemistry for a Sustainable World." San Francisco, CA, April 2010
  - 241st ACS National Meeting, Phoenix, AZ, April 2011.
  - 242nd ACS National Meeting, Denver, CO, August 2011.
  - The Materials Research Society, November 11/30-12/4, 2009, Boston, MA
- NREL published technical papers in prestigious journals (see publication list)
- NREL made numerous presentations (see presentation list) at various conferences

NREL is fully versed in the technical and management issues for H_2 storage material development and has adjusted our R&D efforts to be fully integrated with HSCoE, DOE, and other efforts to maximize DOE funding and accelerate development.

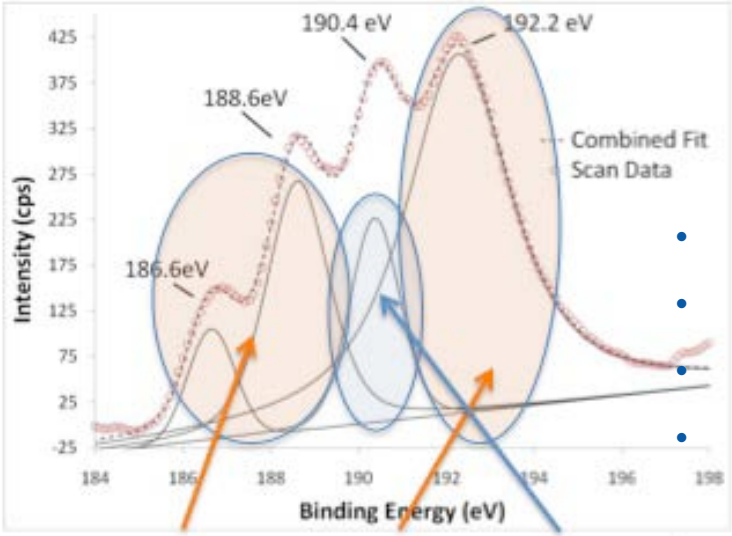
Technical Accomplishments and Progress: Binding Energy

Multiple Routes to BC_x: Templating and Pyrolysis

TEM of Templated BC_6



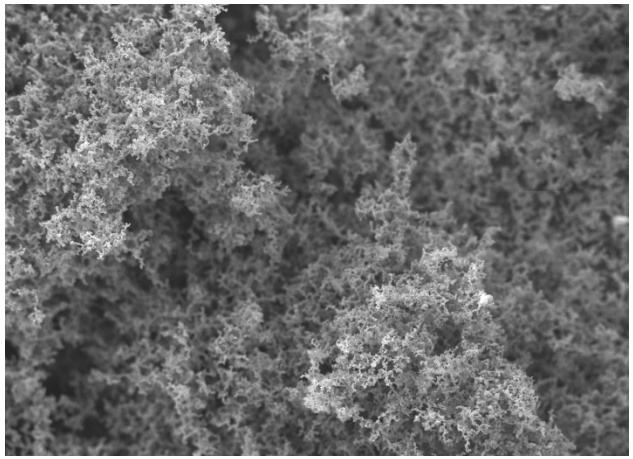
Base CM-Tec



XPS DATA

- 186.6eV = B_4C
- 188.6eV = boron (B-B)
- 190.4eV = sp^2 boron
- 192.2eV = boron oxides

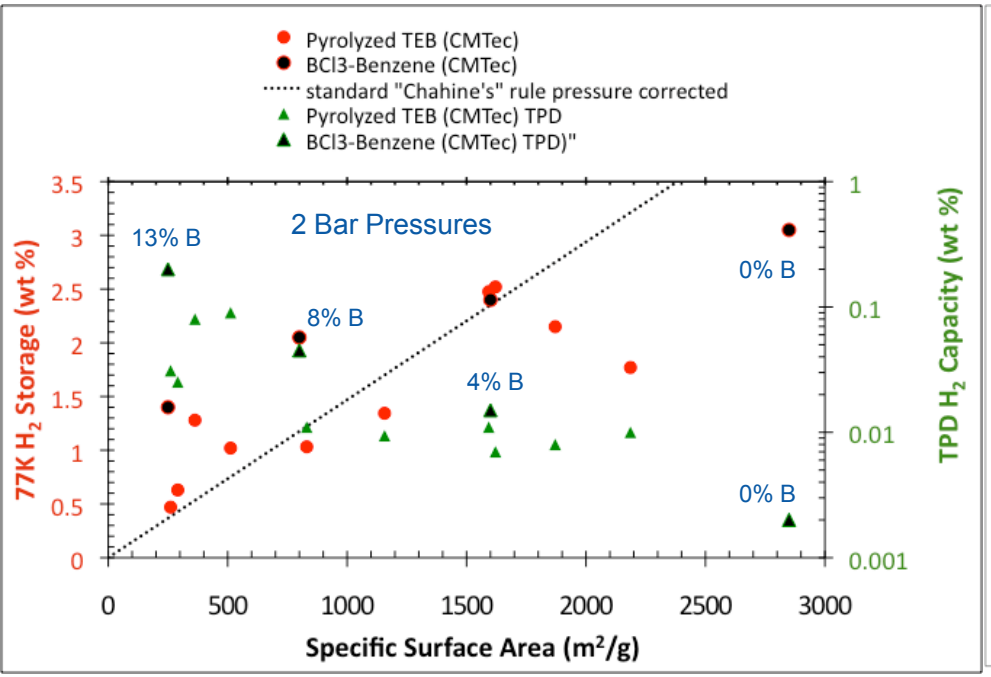
SEM of Pyrolyzed TEB (BC_6)

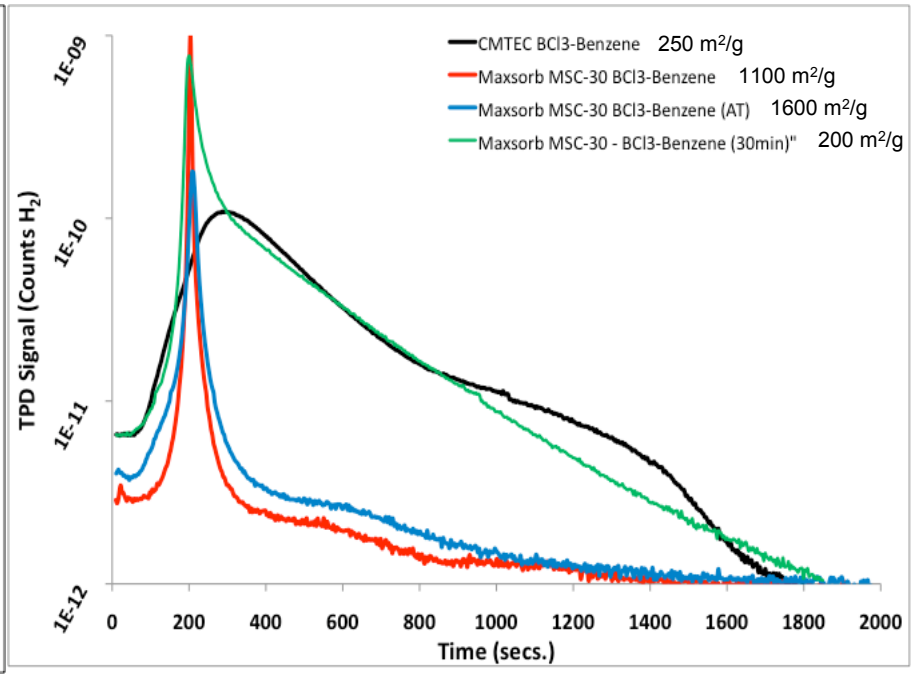


- Templating: $2BCl_3 + C_6H_6 \rightarrow BC_x + 6HCl$ (x = 3-6)
  - Turbostratic morphology from "puckering" of B sites ➔ larger d spacing of graphite planes
  - Routes identified to eliminate Cl poisoning of B sites
- Pyrolysis reactions require no template, avoid halogens of triethylborane (TEB): $(CH_3CH_2)_3B$ + heat ➔ $BC_x + B_nH_x + H_2$

Identified reactions and conditions that favor production of sp^2 B sites relative to B sites that are "inactive" for H_2 adsorption such as :boron, carboranes, boron oxide, boron carbide, etc.

Technical Accomplishments and Progress: Hydrogen Sorption Properties of New BC_x Materials



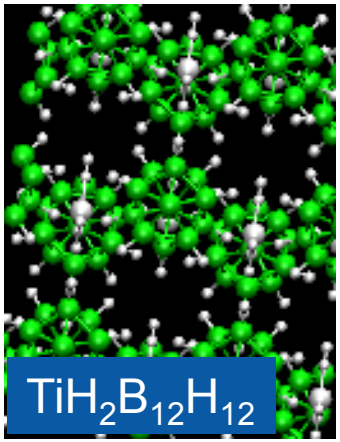


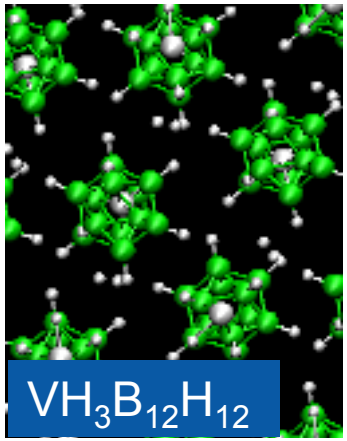
Templated BC_x on CM-Tec Activated C from BCl_3 and TEB

- 2 Bar Cryogenic capacity (77K - Sieverts) much higher than expected for low surface area
- Dramatic enhancement (100 x) of capacity in absence of overpressure (TPD) ➔ potential high energy binding sites
- Cryogenic Sieverts storage increases as a function of boron content
- TPD storage decreases as a function of surface area
- Observed slow kinetics of desorption

Through improved experimental control of surface area, these new BC_x materials show significant promise for high capacity adsorbents with enhanced binding energies

Technical Accomplishments and Progress: New Sorbents Starting with Known Synthesized Materials

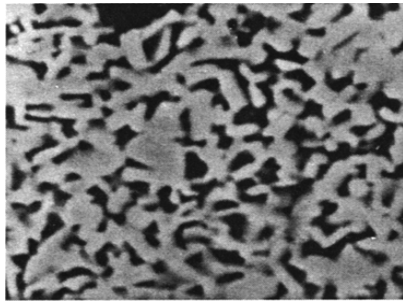




H-rich compounds derived from $CaB_{12}H_{12}$

$MH_xB_{12}H_{12} \leftrightarrow MB_{12} + (6+x/2)H_2 + \Delta H$
M = Ca, Sc, Ti, V; x = 0, 1, 2, 3

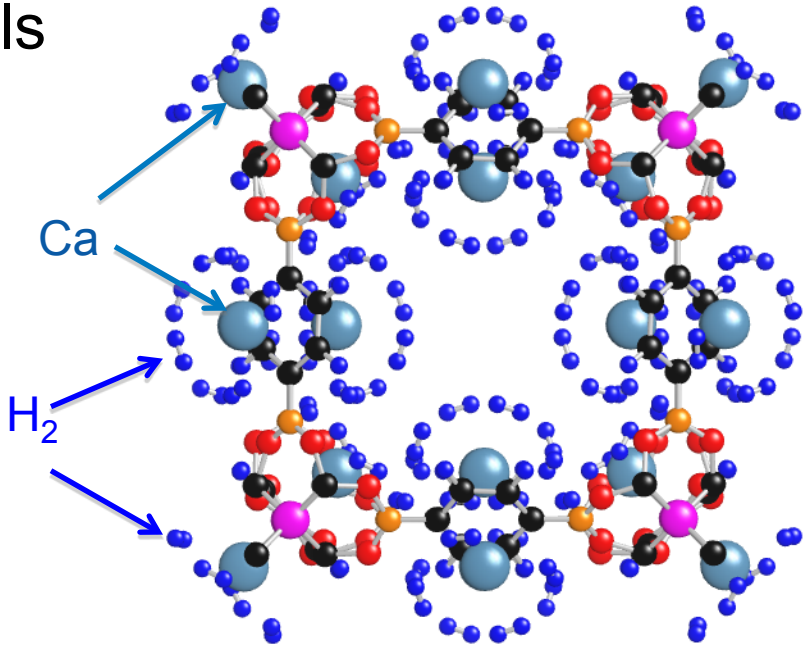
ΔH = 160 ~ 200 kJ/mol-H_2 for Ca
35 ~ 50 kJ/mol-H_2 for Ti, V



Synthesized TiB_{12}

Lepakova et al., *Inorganic Materials 36, 568* (2000)

Tuning H binding energy in $MB_{12}H_{12}$: possibly a new receptor for RT hydrogen sorption.



Ca-Decorated COF for H_2 Storage

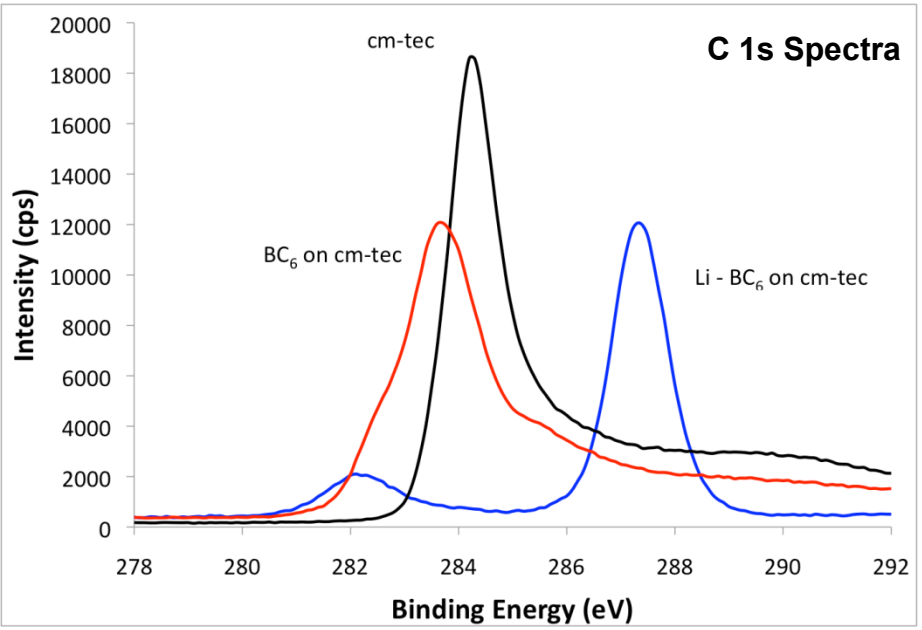
Key Findings:

- **5.6 wt% and 44 g/L**
- **Average binding energy 0.15 eV/H_2**
- **New sorbents designed to be synthesizable and able to meet DOE 2015 Hydrogen Storage Targets**

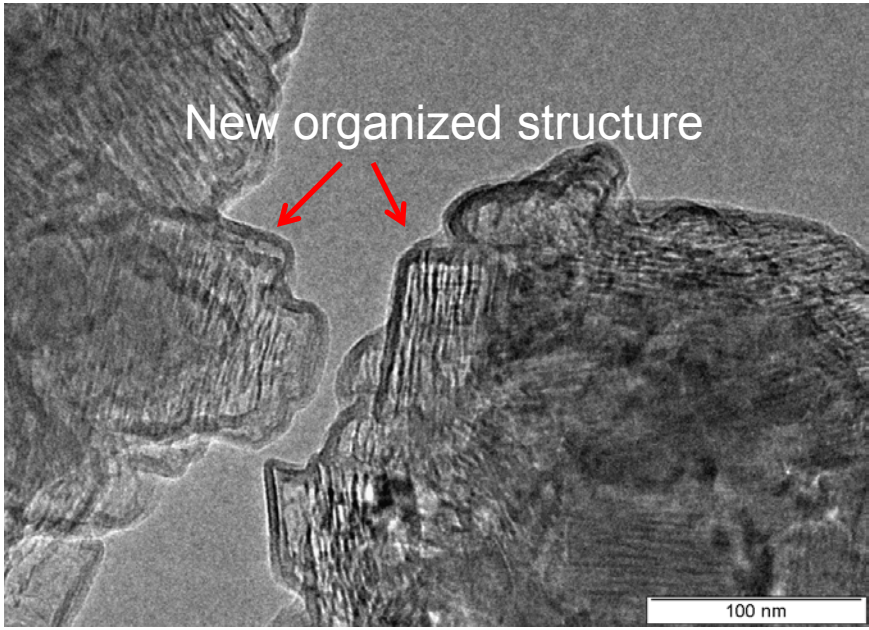
Technical Accomplishments and Progress: Stabilization of Li on BC_6 Supported Materials

- B-doped activated carbon (BC_6) was readily lithiated by reacting in a THF solution of Li naphthalide, successfully scaled-up synthesis.

XPS Data



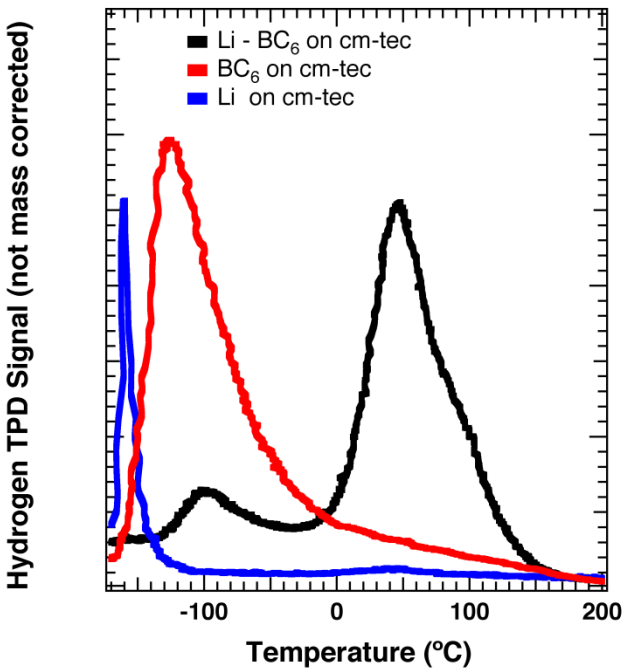
TEM



Shift in the C 1s spectrum indicates possible enhanced substrate interaction in the presence of Li

XPS and TEM suggest significant chemical and structural modifications of the parent BC_6 supported material. These modifications demonstrate the predicted importance of the metal - substrate interactions in enhancing the binding of H_2.

Technical Accomplishments and Progress: Stabilization of Li on BC_6 Supported Materials: Enhanced H_2 Binding



- TPD measurements revealed the reversible desorption of H_2 at < 50 °C following 25 °C H_2 exposure, limited formation of LiH, LiOH.
- Initial high pressure hydrogen adsorption measurements on the lithiated BC_6 material at 100 bar and 30 °C are ~1.5 times greater then the parent BC_6 material
- Hydrogen desorption temperature increased from -120 °C to 60 °C.
- SSA of Li – BC_6 was only **5 m^2/g**

Successfully incorporated Li into a supported BC_6 material. TPD measurements are consistent with NREL theoretical predictions, i.e., the B sites appear to provide well-defined Li metal binding sites. This enables enhanced H_2 binding. 0.52 wt% H_2 adsorption observed at 30 °C and 100 bar for 5 m^2/g SSA.

Results demonstrate that theoretical predictions are relatively accurate and therefore other designed materials when synthesized (e.g. Ca-graphite) should have capacities sufficiently high to be able to meet DOE 2015 or Ultimate Hydrogen Storage Targets.

Technical Accomplishments and Progress: Measurements

Established Comprehensive Capabilities

•Provide a comprehensive hydrogen-storage materials resource for DOE & center partners (Over 7200* measurements performed at NREL over 5 years)

- High Pressure Sieverts (2 instruments, up to 200 Bar)
- Low Pressure Sieverts (high through-put for screening)
- Temperature Programmed Desorption (high sensitivity)
- Specific Surface Area (critical for sorption materials)
- Degas/Anneal (3 stations each with mass specs.)

• Considerable effort to develop expertise and protocols

- Measurement Accuracy

- Developed unique abilities to measure small samples accurately. This is extremely valuable to accelerate new material synthesis/development (lower limit: 1-20 mg depending on technique)
- Improved the protocols for calibration, measurement, throughput & data analysis on several techniques (e.g. Sieverts, TPD, BET, Degas)

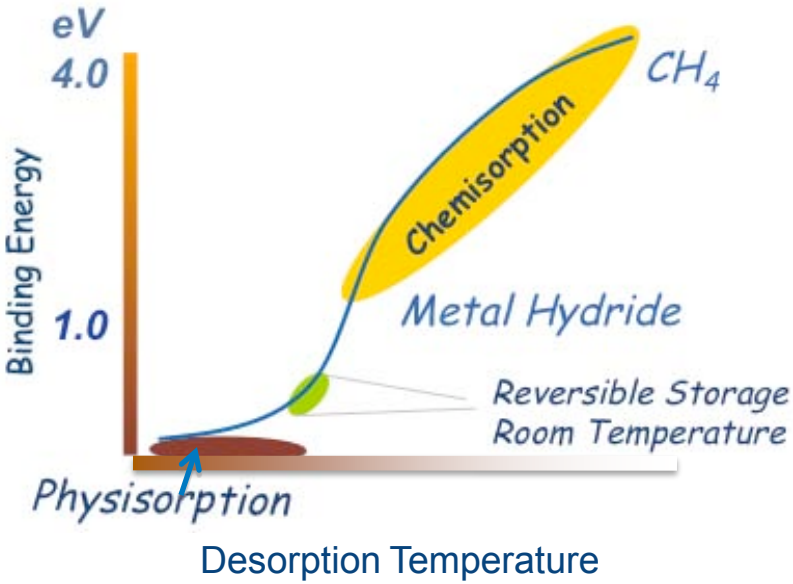
• Creation of "Best Practices" Document

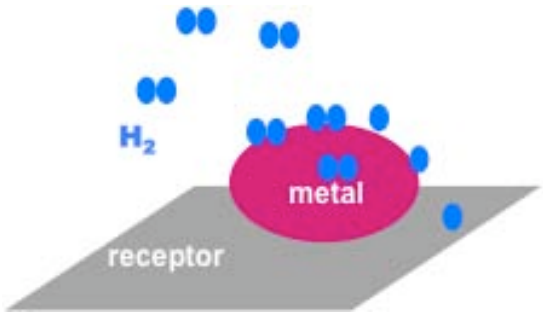
- Subcontract with H_2 Technology Consulting LLC/Karl Gross
- Comprehensive document providing best practices for H_2 storage materials characterization
- Contributions from many H_2 storage experts
- Topics covered: Introduction, Kinetics, Capacity, Thermodynamics & Life Cycle
- "*Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials*" K.J. Gross, et al., (2009) V2-64 U.S. D.O.E. Hydrogen Program document

http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf

NREL further improved measurement capabilities to provide accurate and unique hydrogen storage materials characterization at high throughput; accelerated development.

Technical Accomplishment: Improving the reproducibility and uptake kinetics of weak chemisorptive (spillover) materials





Reversible room temperature hydrogen storage on metal-doped carbon materials, via a **"spillover"** mechanism, involves a series of steps:

- Molecular H_2 dissociates on the metal catalyst particles
- Atomic H migrates to the carbon support
- Diffusion of atomic H across the carbon surface

Determine the best substrate as defined by *chemical composition and porous structure*, for both surface and bulk, that maximizes surface area utilization for hydrogen sorption with acceptable kinetics.

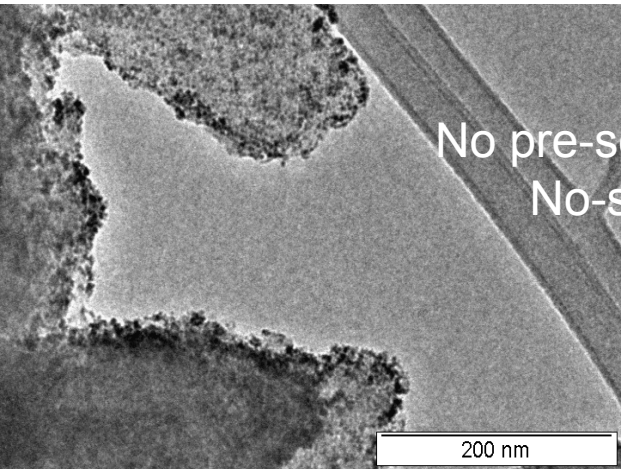
Spillover is a well documented effect that enables rapid ambient temperature hydrogen sorption. Applications possible for vehicle Hydrogen storage once the mechanisms are fully understood and the capacities optimized.

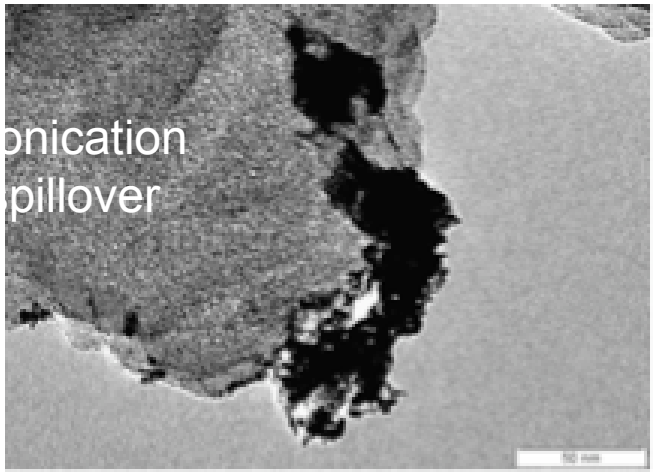
Technical Accomplishment: Improving the reproducibility and uptake kinetics of spillover materials "Key experimental issues"

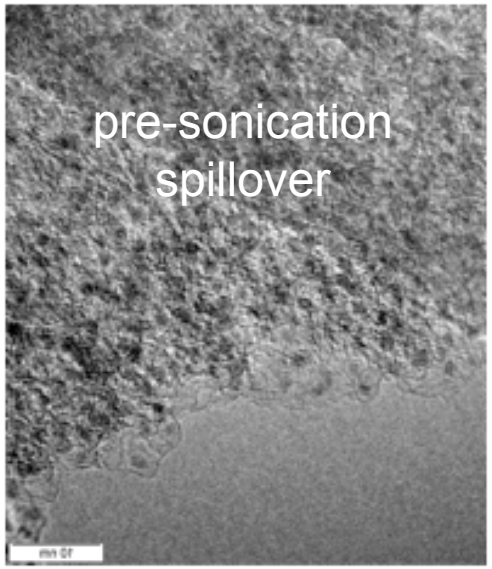
Synthesis

1. Particle Size and Dispersion

- > 2-3 nm reduces enhancement of spillover efficiency; size correlates with correct crystal face?
- Homogeneous dispersion necessary to maximize capacity and kinetics
- (1) and (2) are greatly affected by surface composition and reactivity.







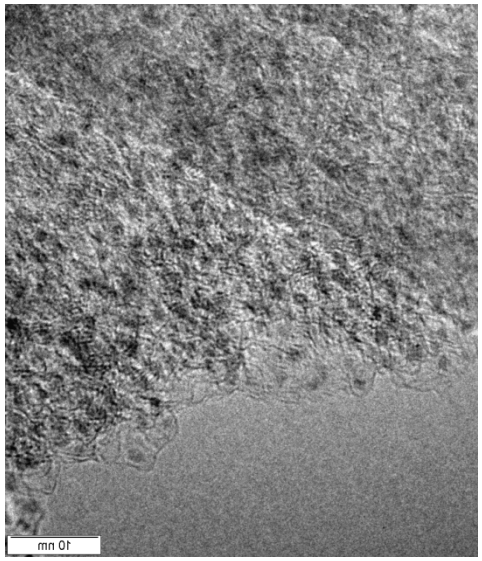
2. Oxygen functionalities

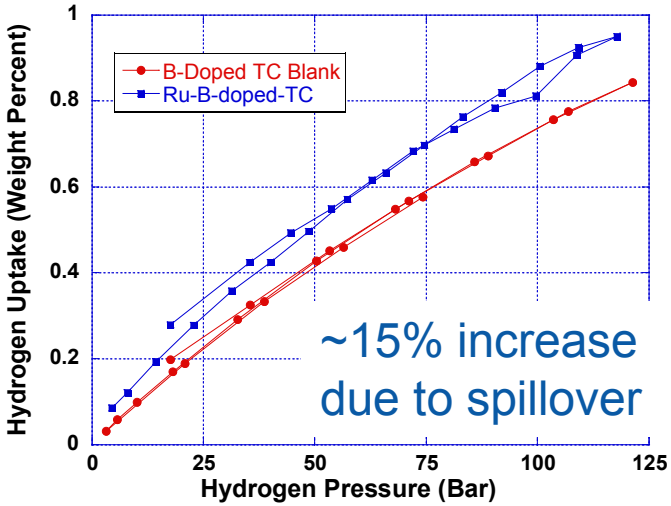
- Oxygenated surfaces predicted to enhance spillover
- On oxygenated carbon surfaces a thermodynamic propensity for water formation, and a small energy barrier suggests that water forms at significant rates during H spillover.
- Formation of *water* has negative consequences on total capacity and the reversibility of hydrogen storage in oxygen modified graphitic materials.

Tight control of materials and processing is essential to reproducible spillover material synthesis and performance; must control surfaces.

Technical Accomplishment: Spillover on BC_x Materials

- Synthesized B-substituted carbon coated CMTec, ~1000 m^2/g.
- 2 nm dia., 8 wt% Ruthenium deposited on material via microwave deposition process.
- Hydrogen adsorption transient occurred at every step in high pressure isotherm.
- Improved kinetics with max adsorption achieved approx 25x faster than similar carbon materials. (95% of adsorption occurred in 10 minutes versus 4-6 hours)





Boron substitutional materials via template (BCx), substantially improves weak chemisorption kinetics and sorption capacity

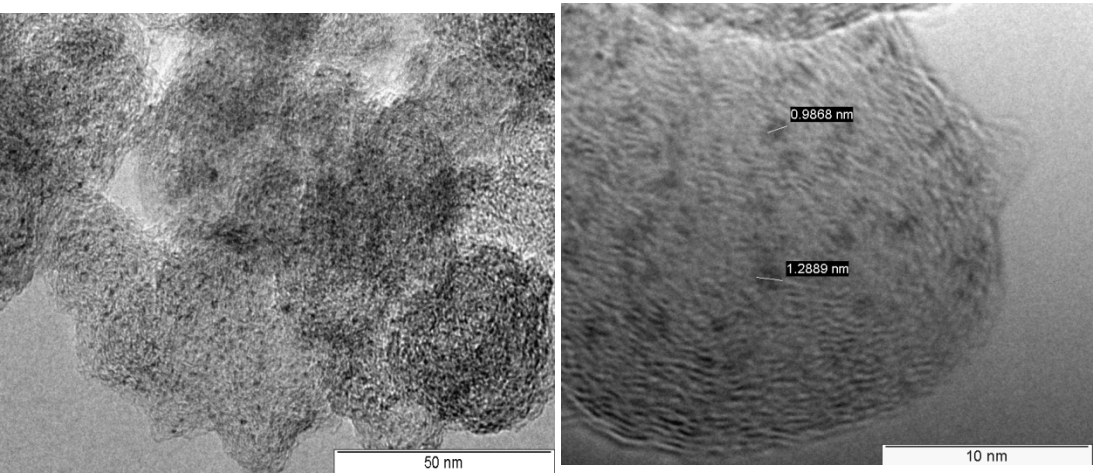
- **Rates substantially faster (10 minutes vs 4 hrs)**
- **Per SSA, ~ 300% higher capacities than expected**
- **Minimal irreversible component**
- **Must perform experiments to determine specific processes involved**

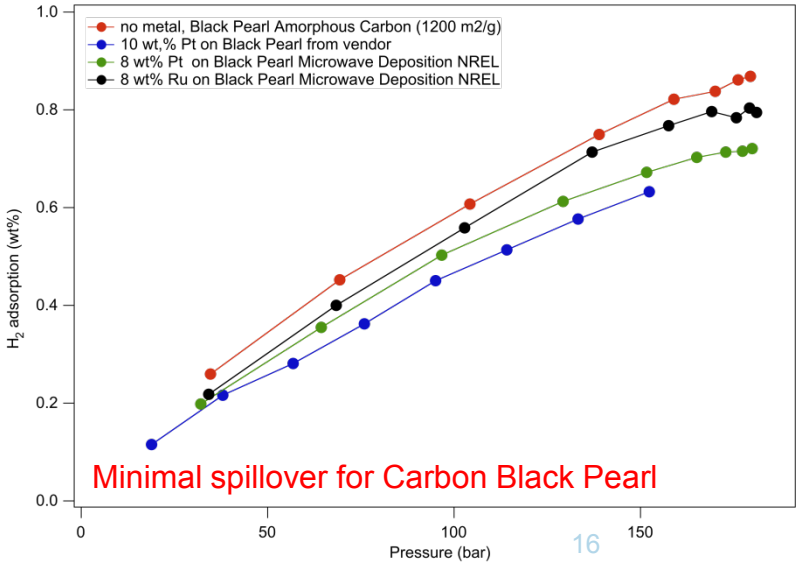
Technical Accomplishment: Spillover Receptor Properties Carbon Black

Receptor material surface functionalization very important
-Dopants and functional groups must be adjusted for optimum spillover,
Especially receptor oxygen groups

- Ru particle dispersion on 1200 m^2/g amorphous carbon black
- While all indications are good that catalyst integration was done appropriately, no significant amount of spillover was detected with Carbon Black.
- This may be due to the complete lack of appropriate oxygen functionalities associated with this material

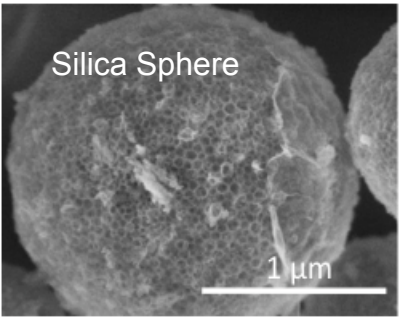
TEM images illustrate appropriate catalyst size and dispersion on Carbon Black Pearl materials.





Technical Accomplishments: Weak Chemisorption of Hydrogen on Pt/ Carbon from Pyrolyzed Sucrose on Silica Sphere Templates

SEM

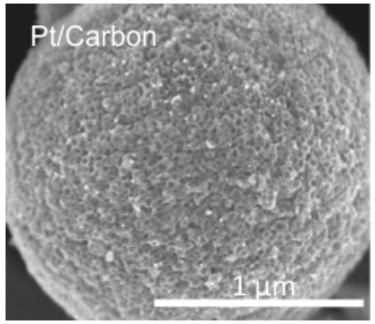


*Pyrolyze sucrose
Platinic Acid, N_2

➔

600-900 °C

SEM



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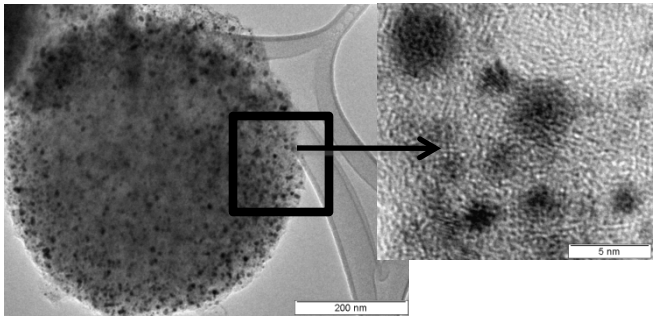
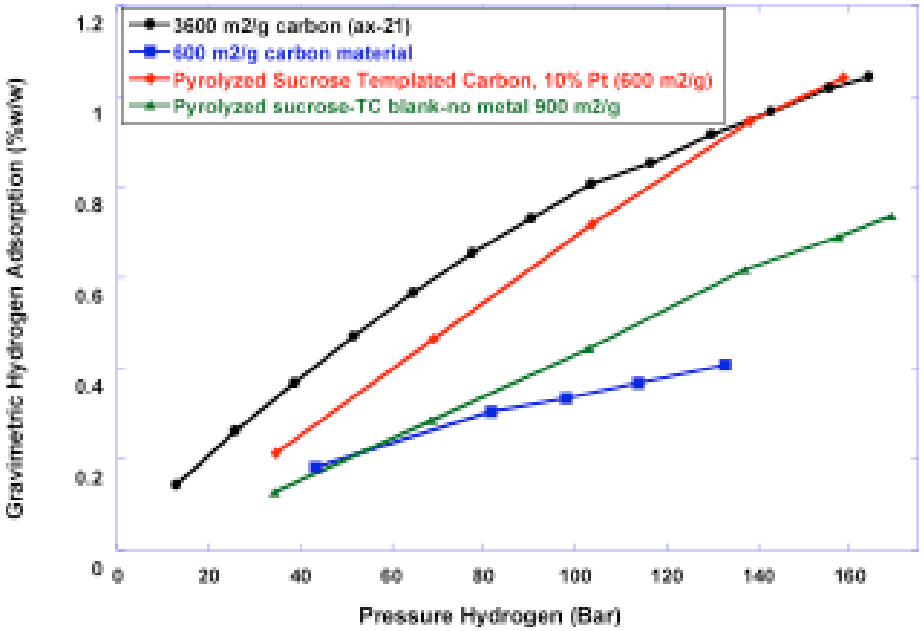


- **Excellent Kinetics: < *5 min to saturation*.**
- **First Pt-Carbon substrate with enhancement of hydrogen adsorption at NREL.**
- **Adsorption of hydrogen still increasing at 150 bar**
- **Minimal irreversibility. Multiple cycles with no loss of sorption capacity or water formation.**
- **Unexpected capacity on "small" surface area, 600 m^2/g**
- **Possibility of "hidden" pore structure needs to be determined**

600 m^2/g, Pt content controlled. (10%w/w)



Identified materials with substantially increase RT sorption rates and sorption capacities. Optimization of these genre of sorbents may meet DOE 2015 storage targets.

**Templated Platinum/Carbon Oxygen Reduction Fuel Cell Electrocatalysts*, S. Pylypenko, T. S. Olson, N. J. Carroll, D. N. Petsev and P. Atanassov, J. Phys. Chem C., 2010, 114(11) 5049

NREL HSCoE Collaborations

As HSCoE lead & leader in H_2 storage materials development & measurements, **NREL collaborates with a large number of groups/institutions around the world**. e.g.

- Works closely with all **HSCoE partners** on a technical and management level
- Works with many **DOE BES projects** on technical and measurement issues, e.g.
  - RPI on development of a more fundamental understanding of physisorption
  - North Dakota State University providing measurements for novel sorption materials
- As part of **HSECoE**, work with several institutions for engineering storage systems
  - Savannah River National Laboratory: Center Lead
  - University of Quebec (Trois-Rivieres), Sorption Task Lead
  - Sorption storage tank analysis and design groups
  - Storage System Working Analysis Group
- **Individual research groups**
  - Work with Karl Gross to develop hydrogen storage measurements best practices
  - Thanos Stubos: Reproduce and validate Demokritos' spillover results using Pd/Hg carbon foam materials for hydrogen storage and assist in improving spillover on these materials
  - Seung-Hoon Jhi, POSTECH, Korea; Hydrogen Storage Materials Modeling
  - CRADA with HSM Systems and the University of New Brunswich to measure light metal hydrides
  - University of Trento, Italy: Develop joint funded effort to produce novel OxyCarbide Derived Carbon (OCDC) porous materials for H_2 storage
  - University of Liverpool: Create joint effort to develop clathrate and other H_2 storage materials leveraging Liverpool's unique combinatorial chemistry systems and NREL's unique measurements capabilities,
  - University of Nottingham: Develop novel templated carbon materials for hydrogen storage,
  - Others include: University of Windsor, Stanford University, Colorado School of Mines, University of Colorado, Virginia Tech, Rochester Institute of Technology, Southwest Research Institute®, University of Delaware. National Aeronautics and Space Administration, Stanford University, University of Quebec (Trois-Rivieres), and other researchers involved in the International Energy Agency and the International Partnership for the Hydrogen Energy.

18

NREL collaborates with dozens of groups throughout the world to accelerate development

HSCoE-NREL: Future Work/Recommendations

FY10: Materials Development and Center Go/No-Go Activities

Wrap up and optimize most promising H_2 storage materials

- **Continue to optimize templating processes to synthesize high surface area materials, controlled nm pore diameters and/or boron concentrations >20%.**
  - Silica and zeolite templates
- **Create stable metal centers** with higher site density and improved dispersion using alkali and alkaline earth materials including Li, Na, Ca,
  - Vapor and chemical deposition of single metal atoms on materials with sites that stabilize the metal atoms.
- Establish the hydrogen sites on BC_x/Li and Pt/Templated silca/zeolite carbon **spillover materials** via various spectroscopies
  - Perform appropriate characterization (IR, Raman, TPD, Neutron scattering, NMR, ESR) as necessary to determine H state on receptor
  - **Scale-up synthesis of most promising materials for round-robin verification of samples**
    - Send grams of material to NIST with and without air exposure to determine site of hydrogen sorption.

Complete BEST Practices document that outlines the state-of-the-art measurement techniques and high-throughput measurement parameters necessary for valid hydrogen measurements

Complete materials selections, recommendations, and Center final report.

- Determine viability of high surface area materials to meet DOE 2010, 2015 and ultimate targets
  - Determine whether high surface area materials with optimum pore size substantially improves volumetric capacity
  - Quantify the enhancements produced by substitutions for dihydrogen binding and metal stabilization
  - Demonstrate the ability to form and quantify the H_2 binding of metal centers and their ultimate storage potential
  - Quantify the potential of weak-chemisorption along with the affects of intrinsic and functionalized material properties

Complete and submit the final report and/or publication(s) for the center

NREL HSCoE Summary

Developed novel scalable synthetic processes, ie templating, to form high surface area lightweight materials with optimum pore structure and composition for H_2 storage. These techniques accelerated development by increasing appropriate material synthesis rates where all the higher H_2 binding energy sites are accessible.

Demonstrated that B substitution in C matrix 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.

NREL identified that barriers to H-migration can be lowered sufficiently to enable spillover via structural and electronic features, where H will diffuse before it desorbs. These result provide development paths to create high capacity, high rate H storage spillover materials that meet DOE targets

NREL developed several new carbon and catalyst processing that improved weak chemisorption ("spillover") capacity and charging rates. The decreased processing time, scalability, and improved kinetic performance should further accelerate the materials development to meet DOE targets.

NREL identified potential issues that produce irreversibility and cause irreproducible hydrogen sorption measurements, especially in "spillover" materials. An improved understanding of surface functionalization, catalyst size and dispersion will enhance various weak/strong sorption processes.

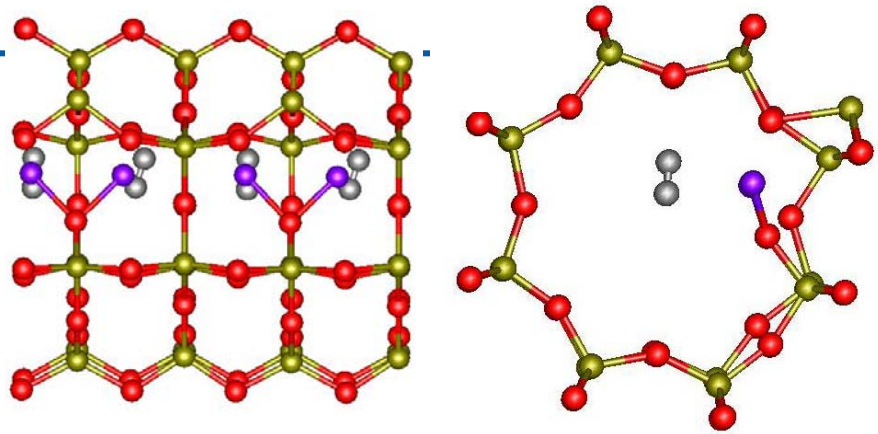
NREL improved measurement capabilities to provide more accurate and unique H_2 storage materials characterization at high throughput. Established in BEST practices document on how to perform and interpret hydrogen storage measurements correctly. Assisted other researchers via validation or non-validation of results.

Theory and experiment continued to iteratively interact to design feasible H_2 storage materials. From the outset 5 years ago, 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.

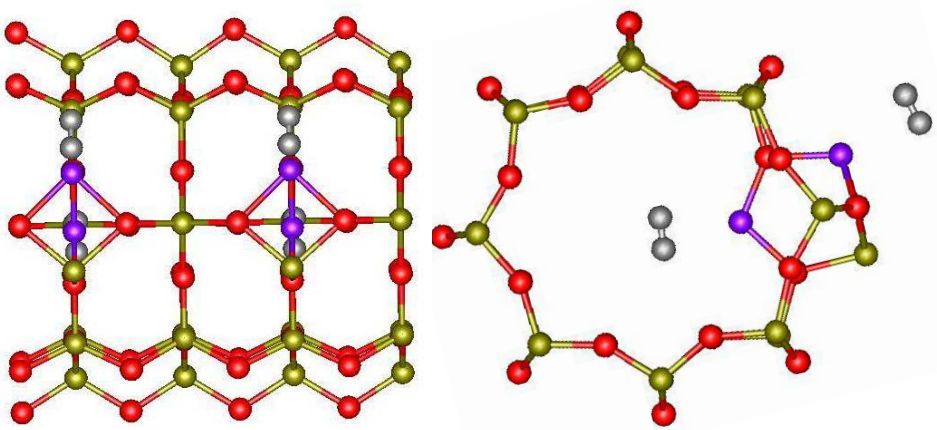
Identified new inexpensive materials that use unique properties of Ca with very viable synthetic routes. These revolutionary new materials could store H_2 at > 100 g/L and > 10 wt%, exceeding DOE's ultimate targets including cost, and volumetric and gravimetric capacities.

Supplemental Slides

Recommendation for Future



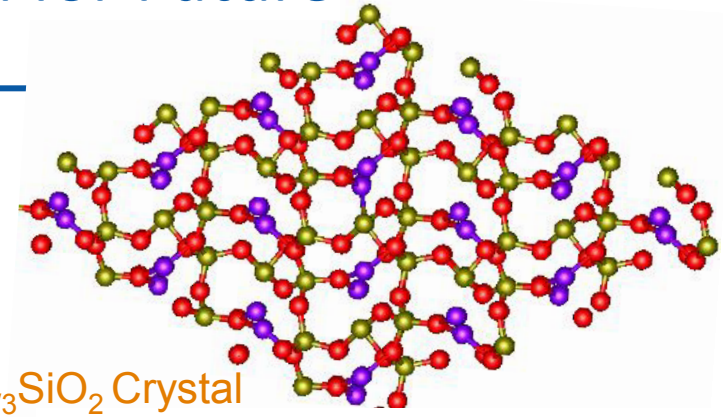
25-26 kJ/mol-H_2



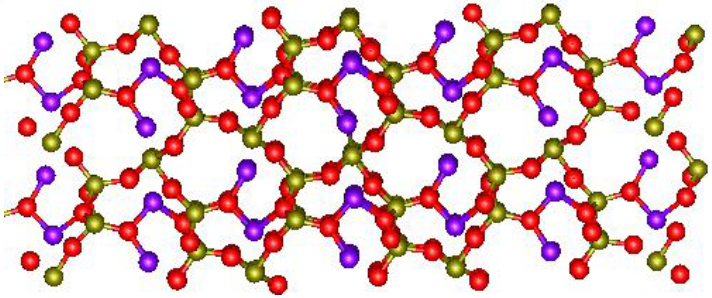
15-26 kJ/mol-H_2

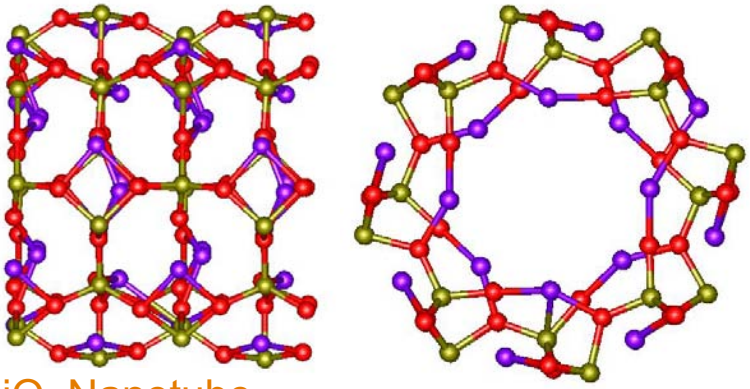
Si O Li H

H_2 Binding to Li-doped Porous SiO_2
Li atoms are fully dispersed and stably fixed.



$Li_{2/3}SiO_2$ Crystal



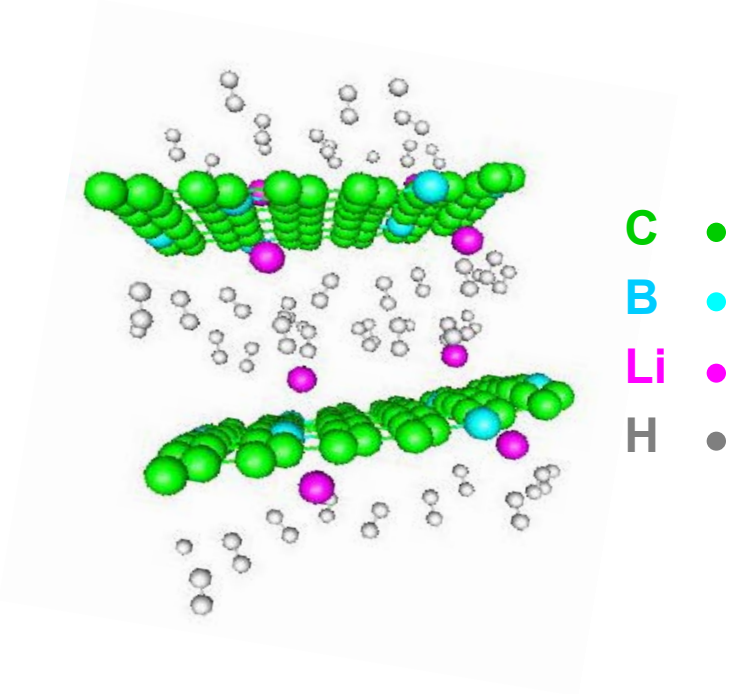


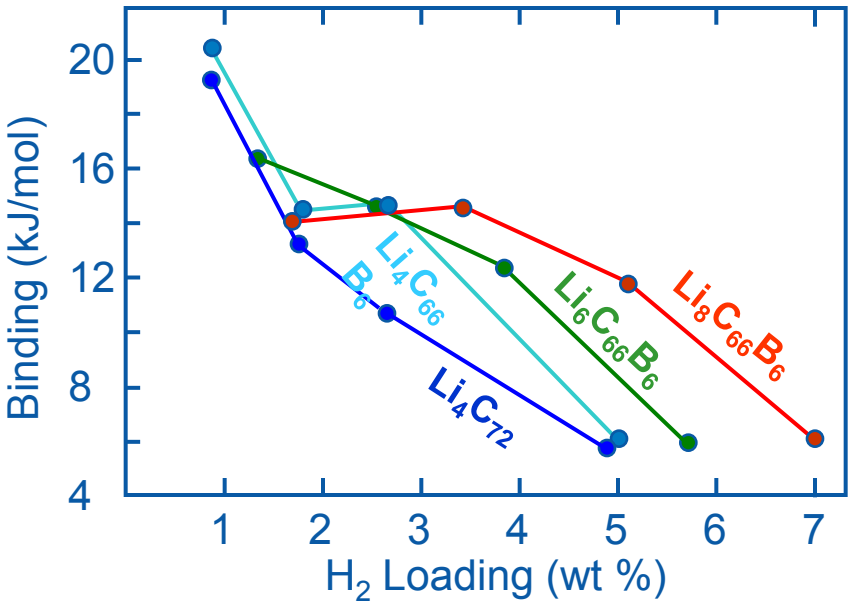
$LiSiO_2$ Nanotube

High-density Li can be dispersed and anchored firmly on in Porous SiO_2

Towards Synthetically Attainable Systems

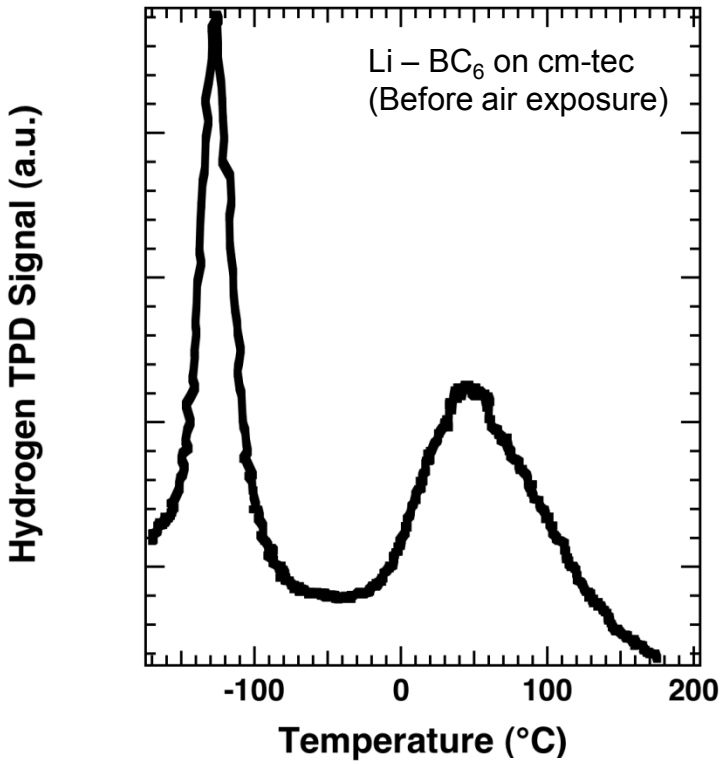
Concept: ***H_2 storage in Li intercalated graphite (Zhao et al. PRB, 2008, 78, 144102)***



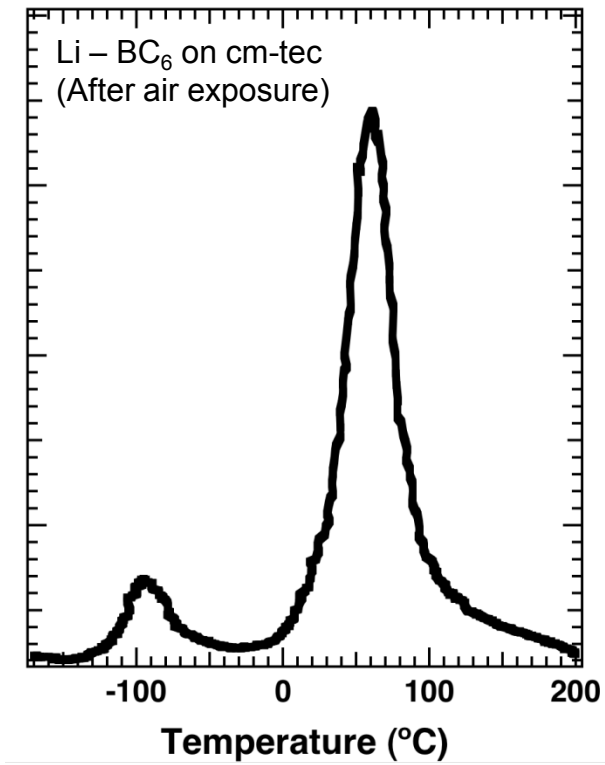


Utilizing the higher Coulomb repulsion between alkali/alkaline metals will facilitate metal - substrate binding. In addition, doping of the substrate with boron will enhance charge transfer between the metal and substrate, enabling a higher Li concentration before metal agglomeration occurs.

Enhanced Stability of H_2 Adsorption Sites in Lithiated BC_6 Materials

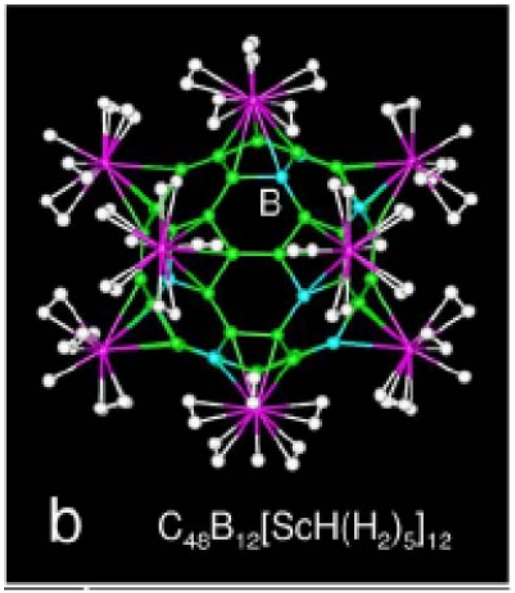


Extended exposure
to ambient conditions



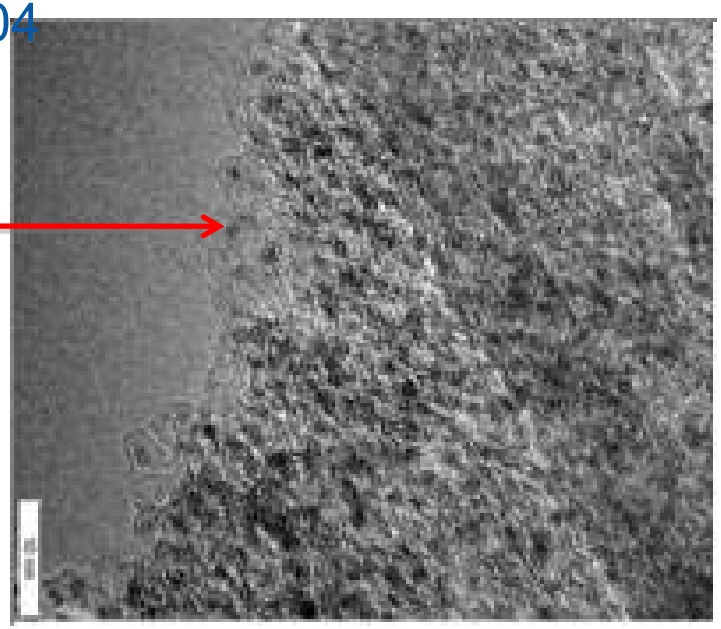
Li – BC_6 materials were able to withstand diverse handling and processing conditions. TPD measurements revealed the reversible desorption of H_2 following exposure to O_2 and H_2O.

Substituted Materials: 5 year Success Story

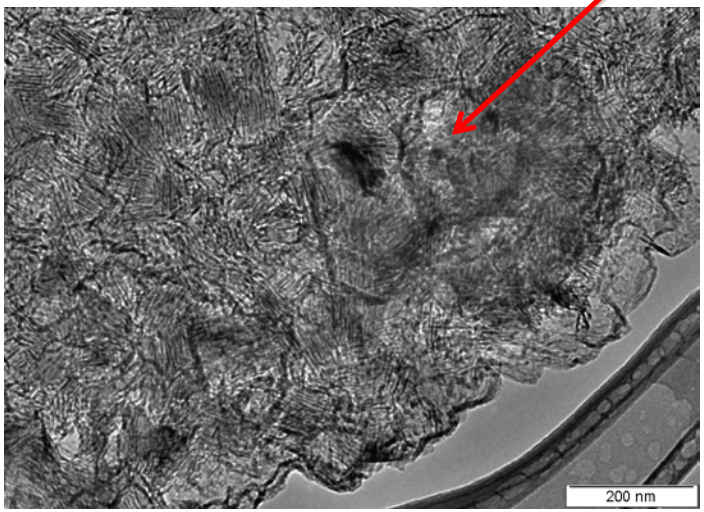


Kim, *P.R.L* (2006), 016102
Zhao, P.R.L. 94, 155504

BC_x- Ru



BC_x- Li



- NREL theory predicted enhanced coordination of transition metal atoms to sp^2 B sites in BC_x
- Syntheses developed for highly dispersed metals on BC_x materials
  - BC_x-Ru
  - BC_x-Li
- BC_x-M systems are best performers to date for spillover and strong binding