

IV.C.6 Weak Chemisorption Validation

Thomas Gennett (Primary Contact), Lin Simpson, Jeffrey Blackburn, Katherine Hurst, Philip Parilla, Chaiwat Engtrakul, Steve Christensen
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401-3393
Phone: (303) 384-6628
Email: thomas.gennett@nrel.gov

DOE Managers

HQ: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

GO: Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@go.doe.gov

Subcontractors:

- University of Hawaii (Craig M. Jensen), Honolulu, HI
- University of New Mexico (Plamen Atanassov), Albuquerque, NM
- Max Planck (Michael Hirscher), Stuttgart, Germany
- Institut de Chimie et des Matériaux (ICPME) (Michel Latroche), Paris, France
- H2 Technology Consulting LLC (Karl Gross), Alamo, CA

Project Start Date: October 1, 2011

Project End Date: Project continuation and direction determined annually by DOE

- Provide highly accurate hydrogen storage measurement support to the sorption community in order to validate exceptional results.
- Coordinate additional work for the Best Practices document and for the characterization of hydrogen storage materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program's Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Weight and Volume
- (C) Efficiency
- (E) Refueling Time
- (M) Hydrogen Capacity and Reversibility
- (N) Understanding of Hydrogen Physi- and Chemisorption
- (O) Test Protocols and Evaluation Facilities

Technical Targets

This project is validating experimentally observed weak chemisorption. Insights gained from this work may be applied toward the future design and synthesis of hydrogen storage materials that meet the following DOE 2017 hydrogen storage system targets:

- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

The specific technical objectives include:

- Verify at least 30% increase in hydrogen uptake over baseline sorbent material at room temperature conditions based on the effects of weak chemisorption/spillover.
- NREL will complete compiling the sorption test results for at least two different materials each prepared by at least two independent laboratories with sorption measurements made for each in at least three separate laboratories. Results will include at least two spectroscopic characterizations for each sample as well. These results are to be compiled into a report for publication either on the DOE Hydrogen and Fuel Cells' website or in a peer reviewed journal by September 30, 2012.

Fiscal Year (FY) 2012 Objectives

- Evaluate the weak chemisorption/spillover process as a means to achieve DOE 2017 Hydrogen Storage goals:
 - Lead sample exchange and measurement validation efforts for weak chemisorption.
 - Perform round robin with "standard" high specific surface area sorbents to ensure all participating laboratories are measuring similar hydrogen storage capacities for both volumetric and gravimetric measurements.
 - Evaluate universal reproducibility of enhanced adsorption weak chemisorption/spillover effects.
 - Determine type of interaction of the carbon-based support with the spillover hydrogen.
 - Establish if weak chemisorption/spillover is a viable process for hydrogen storage.
 - Communicate validated results to the community at large.

Accomplishments

- Completed synthesis of three different spillover samples and distributed to the different labs for evaluation.
 - Verified a >30% enhancement of hydrogen storage in Pd catalyst on templated carbon (Pd/TC) materials via volumetric measurements (NREL and ICPME).
- Synthesized and characterized weak chemisorption/spillover materials at four different laboratories (NREL, ICPME, Max Planck, Penn State)
- Demonstrated direct spectroscopic evidence of a reversible room temperature sorption/desorption apparently from a unique C-H interaction via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and nuclear magnetic resonance (NMR) spectroscopies.
 - DRIFTS measurements up to 100 bar hydrogen overpressure for Ru-BCx (BCx is a boron-substituted carbon material formed by the pyrolyzation of triethylborane) and Pd/TC showed a unique reversible infrared stretch that was tentatively assigned to spillover hydrogen.
 - NMR measurements of the Ru-BCx and Pd/TC showed reversible room temperature carbon substrate-hydrogen interaction upon exposure to up to 100 bar hydrogen overpressure.
- Reported detailed findings and recommendations on hydrogen spillover results.
 - International Energy Association Hydrogen Implementation Agreement (IEA-HIA) Task 22 meetings in Copenhagen Denmark and Heidelberg Germany.
 - DOE Fuel Cell Technologies Annual Merit Review, Washington, D.C.
 - Ceramic Society Materials Challenges in Alternative and Renewable Energy, March 2012.
 - Session organizer and presenter at American Chemical Society Meeting, (August 2011) and IEA-HIA Task 22 Hydrogen Storage Meeting (September 2011).
 - Annual Hydrogen Storage Tech Team presentation April 2012.
- Completed required deliverables for the Best Practices document.
- Submitted for publication five separate peer-review journal articles related to our efforts.



Introduction

The ultimate goal of the Hydrogen Storage sub-program is the development of hydrogen storage systems that meet or exceed the DOE's goals for the onboard hydrogen storage in hydrogen-powered vehicles. With the tremendous interest in weak chemisorption materials for hydrogen storage, NREL and DOE have dedicated considerable resources working with partner institutions to synthesize specific materials and to develop/perform the requisite measurements in order to establish the capacity, kinetics and overall performance of these materials. The key critical issues that must be resolved for these materials include reproducibility of material synthesis, understanding the kinetics of H transport on receptor surfaces, and which chemical reactions are desired and which are not. In addition, weak chemisorption properties are intricately linked to more standard H₂ storage mechanisms, so information gained on the hydrogen-substrate interactions should help accelerate viable sorbent development.

Approach

Organized and led an international group with IEA and International Partnership for the Hydrogen Economy members to validate weak chemisorption synthesis and measurement results. This past year participants included: Angela Lueking (Penn State), Michael Hirscher (Germany), Michel Latroche (France), Thomas Gennett (NREL), Craig Brown (National Institute of Standards and Technology), Craig Jensen (University of Hawaii), Mike Miller (Southwest Research Institute®) and Channing Ahn (California Institute of Technology). Our approach included the synthesis and characterization of a series of materials with an unexplained enhancement of hydrogen sorption in the presence of catalysts that is thought to be caused by hydrogen spillover. The materials selected are Pd/TC, Pt/TC, and Ru/BCx. These materials were synthesized and validated across laboratories. As we move forward we will utilize volumetric measurements for verified capacity measurements. Then through spectroscopic evaluation of the materials with DRIFTS and NMR we will determine correct peak assignments in order to determine if spillover hydrogen spectroscopic modes are in regions expected for room temperature hydrogen desorption. There will then be a coordination of efforts for Inter-laboratory comparison of characterization of results and eventually a reconciliation of spillover propagation mechanisms to thermodynamic parameters.

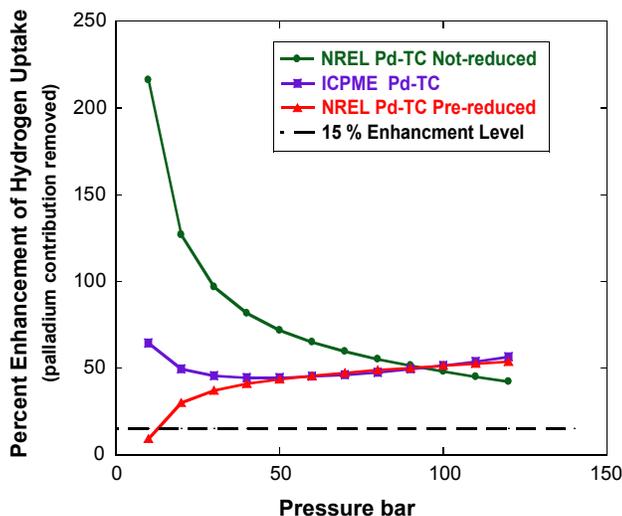
Results

1. Confirmed hydrogen sorption enhancement in Pd/TC materials of greater than 30% enhancement. NREL and ICPME were able to achieve a similar enhancement in

hydrogen sorption on Pd incorporated into a TC matrix. This adsorption was beyond that expected for palladium hydride formation, Pd-H₂, possibly from the addition of the Pd. This was confirmed on two separate samples (Figure 1).

2. DRIFTS determination of new hydrogen-substrate interactions for an apparent spillover material. Using

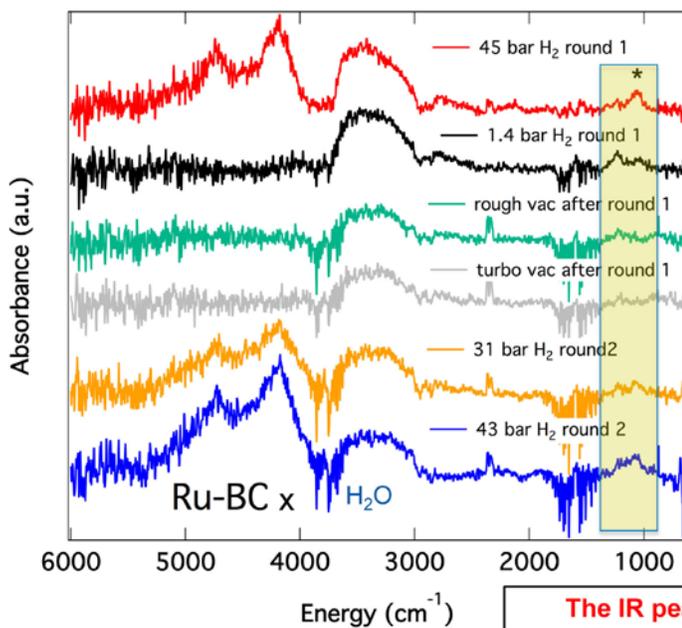
infrared spectroscopy to identify distinct substrate-hydrogen interactions is an essential component of our work as we look to establish the energetics associated with the spillover hydrogen. Figure 2 shows DRIFTS spectra for several samples charged with molecular deuterium and treated at various temperatures.



- greater than 45 percent increase in hydrogen uptake over baseline sorbent material at room temperature conditions is demonstrated.
- Data from two separate laboratories (purple and red traces) are shown.
- false enhancement can be observed when the metal oxide is initially present in the Pd-TC materials (green isotherm).

A multi-laboratory verification of a reversible enhanced hydrogen sorption via spillover at room temperature

FIGURE 1. Multi-laboratory comparison of volumetric data which illustrates a greater than 45% reversible hydrogen sorption enhancement attributed to a possible “spillover” type process



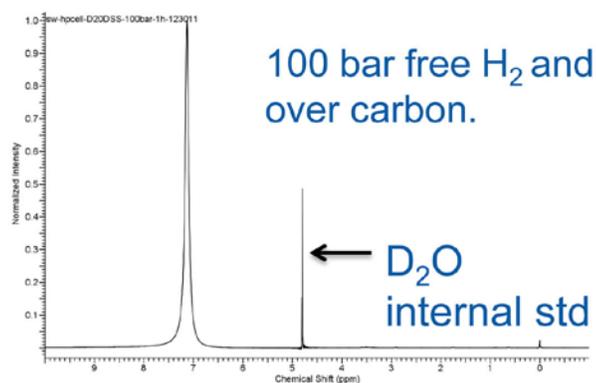
- Sample degassed To 250 °C
- First dose shows water formation similar to observed with TPD
- Upon evacuation, peaks at 1070 and 1230 cm⁻¹ “disappear”
- No degas prior to second dose.
- Peaks reappear at 1070 and 1230 cm⁻¹

The IR peaks, apparently from spillover process, are reversible

FIGURE 2. DRIFTS spectra for RuBCx sample which illustrates the reversibility of the new C-H peaks that appear in the infrared spectrum

3. ^1H NMR evidence for spillover hydrogen on a Ru-BCx material. NREL synthesized over 4 grams of ruthenium-decorated BCx TC materials and out of that batch both DRIFTS and NMR experiments were performed. The NMR results are illustrated in Figure 3. This unique peak shape is currently undergoing deconvolution to establish the type of carbon substrate-hydrogen interaction.

4. In August 2012, we will initiate synchrotron spectroscopic investigation of hydrogen-matrix interactions on the Ru-BCx sorbent in order to ascertain optimized storage capacity limits. Through a successful competitive proposal we have been awarded access to the Stanford Synchrotron Radiation Laboratory/Stanford National Accelerator Laboratory facility at Stanford University. With the use of our model materials system, it will be the most sensitive to changes in sp^2 to sp^3 bonding and will enable X-ray absorption spectroscopy and X-ray emission spectroscopy. These measurements can be correlated with states in the metal of choice regarding hydrogen adsorption, dissociation, and migration.



Signal shifted upfield 2.2 ppm (from 7.1 to 4.9 ppm) Chemical shift and broadening indicate physisorbed H_2 interacting with BCx.

NMR Signal is reversibly split on RuBCx with hydrogen dose as compared to BCx blanks

No new signals observed for ^{11}B NMR.

Possible new reversible C-H interaction observed

Conclusions and Future Direction

- Reconcile spillover propagation mechanisms:
 - Reconcile mechanism with metal-mediated processes with different substrate matrices.
 - Investigate new weak bond or localized catalytically activated interaction.
 - Use metal dispersion effects to establish whether current enhancements are localized or if there is evidence of long-range interactions.
 - Determine specifics of new C-H interaction on RuBCx material through currently on-going Stanford Linear Accelerator Center investigation.
- Determine ultimate spillover capacity possible with optimized interactions and substrate chemistry:
 - Evaluate effects of pore structure.
 - Design materials to enhance diffusion across substrate surface away from metal sites.
 - Determine whether PdBCx shows comparable enhancement to Pd/TC.

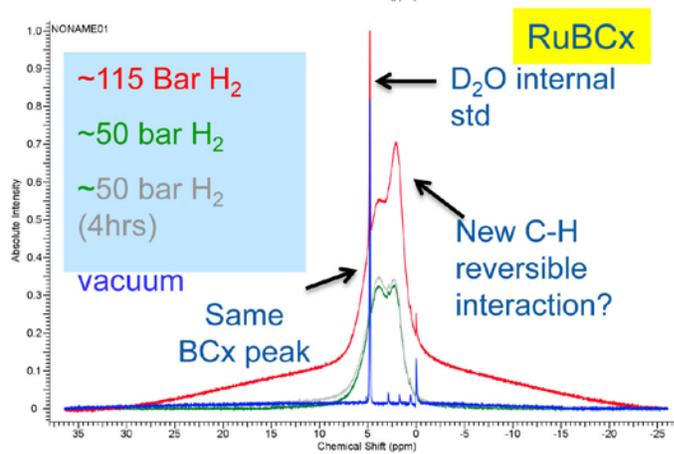
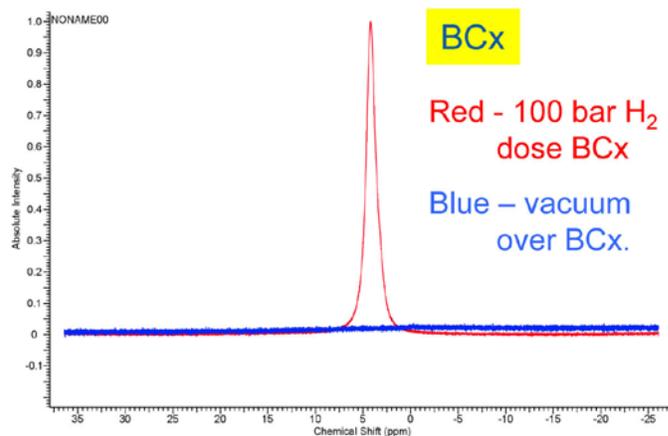


FIGURE 3. ^1H NMR data of BC_x material that illustrates the appearance of a new C-H interaction upon exposure of the sample to hydrogen overpressures at room temperature

- Establish ability to quantify hydrogen adsorption via DRIFTS and/or NMR spectroscopic techniques:
 - Investigate whether or not volumetric enhancements match new spectroscopic data.
 - Analyze Pd-TC and Pd-BCx materials via DRIFTS and NMR.
- Expand NMR work:
 - Deconvolute the observed features resultant from room temperature hydrogen sorption.
 - Perform variable temperature analysis of the BCx samples to verify the dynamic behavior.
 - Characterize the features in the RuBCx spectrum:
 - Quantification by line fitting
 - Characterization by T_1 analysis
 - Further analysis by study of ^{13}C -labeled materials with magic-angle-spinning solid-state NMR
 - Coupling constant and off resonance analysis.
- Complete the remaining sections, and update the other sections within Best Practices document.
- Stanford Linear Accelerator Center Work
 - Study, as a function of H_2 over-pressure, the sorbent near edge X-ray absorption fine structure (NEXAFS) via X-ray Raman scattering.
 - Correlate changes in the unoccupied density of states (from the NEXAFS) that support a transition away from sp^2 towards sp^3 bonding upon hydrogen uptake.
 - Probe the chemical states of the metal catalyst as a function of H pressure using X-ray emission spectroscopy.
 - Establish the experimental characterization protocol to determine the optimized reversible room temperature hydrogen capacity for a matrix based upon the results from the Stanford Linear Accelerator Center
- **Report detailing findings and recommendations at:** Tech Team update, (October 2012), Final analysis and recommendations will be presented at the 2013 Annual Merit Review Meeting and within several peer-reviewed journal submissions.

Validation and recommendations of weak chemisorption processes from this project will enable the hydrogen sorption community to accelerate development of room temperature hydrogen storage materials for light-duty vehicle and other early market applications.

FY 2012 Publications/Presentations

Publications

1. “Accelerating the Understanding and Development of Hydrogen Storage Materials: A review of the five year efforts of the three DOE Hydrogen Storage Materials Centers of Excellence.” K. Ott, L. Klebanoff, L.J. Simpson and N. Stetson. Submitted Metallurgical and Materials Transactions A (2012).
2. “Hydrogen Sorption Center of Excellence Final Report,” Lin Simpson Director, April 2012, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/hydrogen_sorption_coe_final_report.pdf
3. “Executive Summaries for the Hydrogen Storage Materials Centers of Excellence; Hydrogen Sorption Center of Excellence Executive Report,” Lin Simpson Director, April 2012, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/executive_summaries_h2_storage_coes.pdf
4. “Critical and precise calibration required to avoid large systematic errors in volumetric apparatus: isothermal case” submitted to *Review of Scientific Instruments*, P.A. Parilla, K.E.Hurst, L.J. Simpson, K.J. O’Neill, T Gennett.
5. “A Dynamic Calibration Technique for Temperature Programmed Desorption Spectroscopy” accepted pending revision to *Review of Scientific Instruments*, K.E. Hurst, M.J. Heben, J.L. Blackburn, T. Gennett, A.C. Dillon and P.A. Parilla.
6. “Spectroscopic Identification of Hydrogen Spillover Species in Ruthenium-modified High Surface Area Carbons by Diffuse Reflectance Infrared Fourier Transform Spectroscopy” submitted to *J. Phys. Chem. C.*, Jeffrey L. Blackburn, Chaiwat Engtrakul, Justin B. Bult, Katherine E. Hurst, Yufeng Zhao, Qiang Xu, Philip A. Parilla, Lin J. Simpson, Craig Brown, Thomas Gennett.
7. “Sodium-Doped Carbon Nanotubes as Potential Hydrogen Storage Materials” C. Engtrakul, C.J. Curtis, L.M. Gedvilas, L.J. Simpson, P.A. Parilla, M.J. Heben, T. Gennett, accepted for publication in *J. Materials Chemistry*.
8. *Manipulation of Hydrogen Binding Energy and Desorption Kinetics by Boron Doping of High Surface Area Carbon*, Justin B. Bult, Justin Lee, Kevin O’Neill, Chaiwat Engtrakul, Katherine E. Hurst, Yufeng Zhao, Lin Simpson, Phillip Parilla, Thomas Gennett, Jeffrey L. Blackburn, submitted to *Chemistry of Materials*.
9. “Synthesis of Novel Lithiated BC_6 Materials with Enhanced H_2 Binding Sites” C. Engtrakul, J.L. Blackburn, J.B. Bult, K.J. O’Neill, P.A. Parilla, T. Gennett, L.J. Simpson. in preparation.
10. “Energetics of hydrogenation of single-walled carbon nanotubes and Graphene” Q. Xu, J.L. Blackburn, L.J. Simpson, T. Gennett, Y. Zhao, in preparation.
11. “Multi-Institutional Comparison of Volumetric H_2 Adsorption Measurements on Carbon Sorbents”, K.E. Hurst, K.J. O’Neill, J.L. Blackburn, T. Gennett, and P.A. Parilla, in preparation.

Presentations

1. Invited Talk: *Weak hydrogen chemisorption validation*, Thomas Gennett, DOE Fuel Cell Technologies Program Annual Merit Review, May, 2012, Washington, D.C.

2. Invited Talk; *Capacity, Kinetics and Evaluation of the Spillover Hydrogen Sorption Process*, Thomas Gennett, IEA-HIA Task 22 Hydrogen Storage, Heidelberg, Germany, May 2012.
3. Invited Talk: “*Capacity, Kinetics and Evaluation of the Spillover Hydrogen Sorption Process*” Thomas Gennett, DOE Technical Advisory Board Meeting, Dearborn, Mi, April 2012.
4. Invited Talk: “*Capacity, Kinetics and Evaluation of the Spillover Hydrogen Sorption Process*” Thomas Gennett, MRS Meeting, San Francisco, CA, April 2012.
5. Invited Talk: “*Capacity, Kinetics and Evaluation of the Spillover Hydrogen Sorption Process*” Thomas Gennett, Materials Challenges In Alternative & Renewable Energy, American Ceramic Society, February, 2012.
6. Invited Talks: Spillover Workshop Winter February 2012, Denver, CO. Organizer and Invited NREL Presentations:
 - a. “*Inter-Laboratory Comparison: Testing Measurement Reproducibility and Accuracy*” Phil Parilla, Katherine Hurst, Lin Simpson, Jeffrey Blackburn, Chai Engtrakul, Thomas Gennett.
 - b. “*Capacity, Reproducibility, and Kinetics of the Weak Chemisorptive (spillover) Hydrogen Sorption Process*, Thomas Gennett.
 - c. *Spectroscopic Identification of Hydrogen Spillover Species in Ruthenium-modified High Surface Area Carbons by Diffuse Reflectance Infrared Fourier Transform Spectroscopy* Jeffrey L. Blackburn,* Chaiwat Engtrakul, Justin B. Bult, Katherine E. Hurst, Yufeng Zhao, Qiang Xu, Philip A. Parilla, Lin J. Simpson, Craig Brown, Thomas Gennett.
 - d. *High Surface Area Boron Doped Carbon with Slow Hydrogen Desorption Kinetics*. Justin Bult, Jeffrey Blackburn,, Kevin O’Neill, Katherine Hurst, Chaiwat Engtrakul, Philip Parilla, Lin Simpson and Thomas Gennett.
7. Invited Talk: “*Capacity, Reproducibility, and Kinetics of the Weak Chemisorptive (spillover) Hydrogen Sorption Process*” Phil Parilla, Katherine Hurst, Lin Simpson, Justin Lee, Jeffrey Blackburn, Chai Engtrakul, Thomas Gennett, IEA-HIA Task 22 Meeting, Copenhagen, Denmark, September, 2011.
8. Invited Talk: *In situ spectroscopic identification of hydrogen binding sites on carbon-based hydrogen sorption materials* JL Blackburn, C Engtrakul, KE Hurst, JB Bult, J Lee, KJ O’Neill, PA Parilla, LJ Simpson, T Gennett 2011 American Chemical Society Fall National Meeting.
9. Invited Talk: *Weak hydrogen chemisorption validation*, Thomas Gennett, 2011 American Chemical Society Fall National Meeting.
10. Invited Talk: *Overview of hydrogen sorbents*; Lin Simpson, Thomas Gennett, Philip Parilla, Jeffrey Blackburn, Chaiwat Engtrakul, Yufeng Zhao, Katherine Hurst, Justin Bult, Kevin O’Neill 2011 American Chemical Society Fall National Meeting.
11. Invited Talk: Common errors found in volumetric hydrogen capacity measurements and how to avoid them Philip A Parilla, Kevin J O’Neill, Katherine E Hurst, Richard Knott, Thomas Gennett, Jeffery L Blackburn, Chaiwat Entrakul, Justin B Bult, Lin J Simpson, 2011 American Chemical Society Fall National Meeting.