

## IV.C.7 Weak Chemisorption Validation

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Project Start Date: October 1, 2010

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

### Fiscal Year (FY) 2011 Objectives

- Evaluate the weak chemisorption/spillover process as a means to achieve DOE 2015 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.
  - Evaluate universal reproducibility of enhanced adsorption weak chemisorption/spillover effects.
  - Determine type of interaction of the 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.
- 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.

### Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program 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 2015 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

The specific technical objectives include:

- Verify at least 15% increase in hydrogen uptake over baseline sorbent material at room temperature conditions based on the effects of weak chemisorption/spillover.
- Via spectroscopic techniques, determine the type of hydrogen-substrate interactions from the enhanced spillover hydrogen using diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), nuclear magnetic resonance spectroscopy (NMR), RAMAN spectroscopy, and neutron scattering.

### FY 2011 Accomplishments

- Completed round-robin analysis of standard samples:
  - Achieved <5% error on hydrogen capacity measurements on the same standard sorbents (two were distributed) at three different laboratories. Completing the standard measurements at three others.
- Completed synthesis of three different spillover samples and distributed the initial set to the different labs for evaluation.

- Verified a >15% enhancement of hydrogen storage in Pd catalyst on template carbon (Pd/TC) materials via volumetric measurements (NREL and ICPME)
- Synthesized weak chemisorption/spillover materials at three different laboratories.
- Demonstrated spectroscopic evidence for spillover C-H bonds.
  - DRIFTS measurements where both Pt-C and Pd/TC showed a unique stretch that was tentatively assigned to spillover hydrogen.
  - Neutron scattering (Ru-BCx), revealed apparent hydrogen wagging modes which correlated to those energies predicted by theory.
  - Reported detailed findings and recommendations on hydrogen spillover results.
    - International Energy Agency Hydrogen Implementing Agreement (IEA-HIA) Task 22 meeting Freemantle, Australia.
    - DOE Fuel Cell Technologies Annual Merit Review, Washington, D.C.
    - Gordon Research Conference, Easton, MA (included a workshop meeting).
    - Pending: American Chemical Society (ACS) Meeting, (August 2011) and IEA-HIA Task 22 Hydrogen Storage Meeting (September 2011).
- Completed four out of five drafts for the Best Practices Document: 515 pgs, seven sections: Introduction, Capacity, Kinetics, Thermodynamics, Cycle-Life, Thermal Properties, Mechanical Properties Measurements.
- Evaluated the hydrogen sorption characteristics of two unique >5,000 M<sup>2</sup>/g high surface area metal-organic frameworks from Northwestern and Texas A&M Universities.



## Introduction

The ultimate goal of the Hydrogen Storage subprogram 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 H<sub>2</sub> 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. Participants include: Angela Lueking (Pennsylvania State University), Michael Hirscher (Germany), Michel Latroche (France), Thomas Gennett (NREL), Craig Brown (National Institute for Standards and Technology, NIST) Craig Jensen (University of Hawaii), Evan Gray (Griffith University), Craig Buckley (Curtin University), Mike Miller (Southwest Research Institute®), Channing Ahn (California Institute of Technology), and Tony Burrell (Argonne National Laboratory).

Our approach includes 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/templated carbon, Pt/templated carbon, and Ru/BCx. These materials are being 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, neutron scattering 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

- **Validation of volumetric analysis of standards across laboratories.** NREL was the lead and distributed a series of samples to various laboratories for testing, Figure 1. As is evident in the isotherms we were able to coordinate and establish an approximate 5% absolute variation in results across six laboratories. The variations in the data were found to be caused by calculation error, skeletal density assumptions and/or null volume assumptions.
- **Confirmation of hydrogen sorption enhancement in Pd-Templated carbon materials.** NREL and ICPME were able to achieve a similar enhancement in hydrogen sorption on Pd incorporated into a templated carbon matrix. This adsorption was beyond that expected for palladium hydride formation, Pd-H<sub>2</sub>, possibly from the addition of the Pd. This was confirmed on two separate samples. A large batch synthesis by ICPME was completed, and those samples are under analysis by other laboratories. NREL is currently synthesizing

Data normalized until the inter-laboratory comparison is complete.

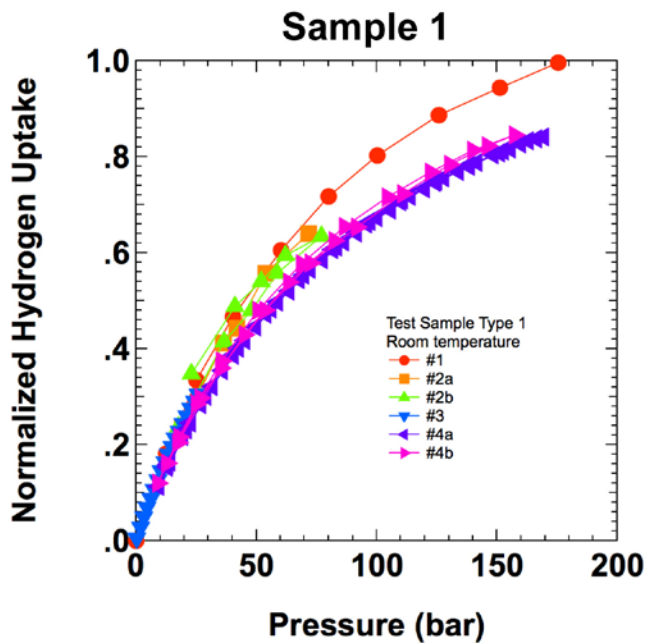


FIGURE 1. Inter-Laboratory Comparison of Volumetric Data for Two Distinct Samples

an independent batch of materials in order to confirm ability to synthesize in two distinct laboratories.

- **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

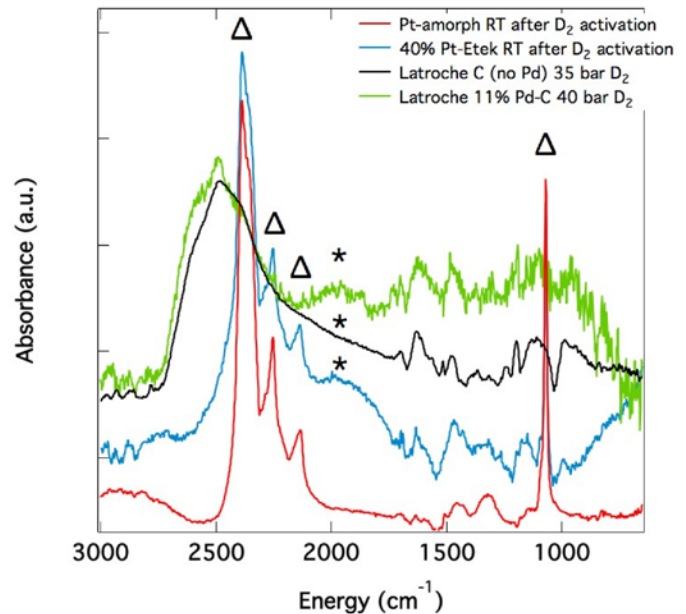


FIGURE 2. DRIFTS Spectra for Various Samples Charged with  $D_2$  at Room Temperature

with the spillover hydrogen. Figure 2 shows DRIFTS spectra for several samples charged with  $D_2$  and treated at two different temperatures. In one experiment, labeled “ $D_2$  activation”, the sample is charged with  $\sim 200$  psi ( $\sim 14$  bar) of  $D_2$  at room temperature, and then heated up to  $200^\circ\text{C}$  in the  $D_2$  atmosphere. The other experiment is simply a room temperature  $D_2$  charge with no heat treatment. Three samples in Figure 2 were subjected to a  $D_2$  activation: an amorphous platinum sample (Pt-amorph), an activated carbon sample with 40% platinum (40% Pt-Etek), and a carbon sample from one of our partners, loaded with 11% Pd (Latroche 11% Pd-C). Interestingly, the  $D_2$  activation procedure yields the same four sharp peaks, labeled by the triangles, for all three of these samples. A group of three sharp peaks occur at  $2,386$ ,  $2,254$ , and  $2,135$   $\text{cm}^{-1}$ , along with an isolated peak at  $1,068$   $\text{cm}^{-1}$ . The three higher energy peaks are in the range expected for surface hydroxyl (O-D) and/or alkane (C-D) vibrations. Because these higher energy peaks are also observed for the amorphous Pt sample, a sample that contains no carbon, the possibility that these peaks are related to the formation of C-D bonds is ruled out. Instead, we propose that these peaks correspond to the possible formation of isolated surface hydroxyl species on the metal nano- or microparticles. Additionally, the isolated and strongly bound nature of the surface hydroxyl species precludes the hydrogen bonding observed for loosely bound water ( $H_2O$  or  $D_2O$ ) that typically results in a broad featureless peak. The narrow peak at  $1,068$   $\text{cm}^{-1}$  would then most likely correspond to a bending motion of the surface-bound hydroxyls. We note that none of these peaks are observed for activation of a carbon sample that contains no metal catalyst.

Finally, we also note that the energies observed for the grouping of peaks in the range of 2,100 to 2,400  $\text{cm}^{-1}$  are significantly higher than what is expected for Pt-D bonds, which are expected to fall in the range of  $\sim 1,688 \text{ cm}^{-1}$ .

For the samples treated with a room temperature  $\text{D}_2$  charge, we evaluated the Pd-TC sample, along with a control carbon sample prepared by the same method, but without Pd incorporation (Latroche C, no Pd). This sample has shown reproducible adsorption capacity enhancement at room temperature, which is presumably due to spillover hydrogen. The main feature observed for the control experiment (Latroche C, no Pd) is a broad absorption feature in the range of 2,000 to 2,800  $\text{cm}^{-1}$ . This feature is assigned to loosely bound  $\text{D}_2\text{O}$  on the surface that most likely forms by the reaction of  $\text{D}_2$  with surface-bound oxygen or hydroxyls. The same broad peak forms for the Pd-containing sample (Latroche 11% Pd-C), but a new broad feature also appears at  $\sim 1,900 \text{ cm}^{-1}$ , which is noted with an asterisk (\*). Interestingly, a similar peak is observed for all samples containing both a catalyst metal and carbon, and not observed for the activated Pt-amorphous sample. Thus, we tentatively assign the broad peak in the range of 1,800–1,900  $\text{cm}^{-1}$  to C-D peaks formed by spillover of deuterium from catalyst particles (Pt or Pd) to the carbon surface. Further experiments must be done to confirm this assignment. Finally, we note the presence of many small peaks in the range of 900 to 1,700  $\text{cm}^{-1}$ . Several of these peaks are similar amongst the samples investigated, while some samples possess unique peaks within the range above. With the recent results from neutron scattering experiments, we are calculating the corresponding infrared energy peak and look for it in this region (900–1,400  $\text{cm}^{-1}$ ) to see if we can correlate the spectroscopic data.

- **Neutron scattering evidence for spillover hydrogen on a ruthenium-BCx material.** NREL synthesized over 4 grams of ruthenium decorated BCx templated carbon materials for neutron scattering studies. The remarkable results are illustrated in Figure 3. This is by far the strongest hydrogen signal NIST has seen for a spillover type material. Interestingly the peaks in the spectrum appear to correspond directly with those predicted by Boris Yakospn at the University of Texas at Austin (private communication). This same sample is now undergoing a series of DRIFTS measurements to verify the peaks with a second spectroscopic method.

## Conclusions and Future Direction

- Complete synthesis of the different spillover samples and distribute round-robin sets to the different labs for evaluation.
- Down select validated spillover materials and distribute samples to other labs for validation and additional spectroscopic characterization. This will include a synthesis of validated spillover materials by other labs.

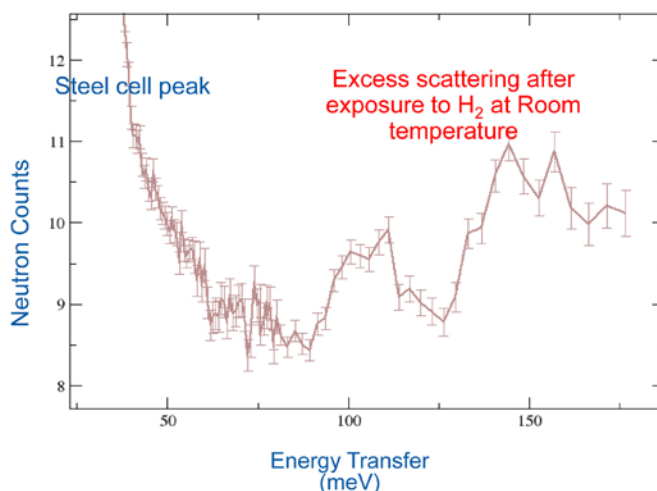


FIGURE 3. Neutron Scattering Data of BCx Material that Contains 6% w/w Ru

- Validate and assign specific types of interactions that have been observed from the spectroscopic evidence for spillover C-H bonds in DRIFTS, and neutron scattering.
- Develop and utilize NMR and possibly near edge X-ray absorption fine structure absorption spectroscopy to further elucidate and confirm the presence of the spillover hydrogen observed in DRIFTS and neutron scattering.
- Complete the remaining section, (Thermal Properties) and update the other sections within Best Practices.
- Report detailing findings and recommendations at ACS Meeting, (August 2011) and IEA-HIA Task 22 Hydrogen Storage Meeting (September 2011), final analysis will be presented at the 2012 Annual Merit Review meeting.

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.

## Special Recognitions & Awards/Patents Issued

1. Jeffrey Blackburn: 2011 NREL Staff award for Scientific Excellence.

## FY 2011 Publications/Presentations

### Publications

1. Solution-Phase Synthesis of Heteroatom-Substituted Carbon Scaffolds for Hydrogen Storage, Zhong Jin, Zhengzong Sun, Lin J. Simpson, Kevin J. O'Neill, Philip A. Parilla, Yan Li, Nicholas P. Stadie, Channing C. Ahn, Carter Kittrell, and James M. Tour; J. Am Chem. Soc. 132, 15246 (2010).



2. Nano-Engineered Spacing in Graphene Sheets for Hydrogen Storage, Zhong Jin, Wei Lu, Kevin J. O'Neill, Philip A. Parilla, Lin J. Simpson, Carter Kittrell, and James M. Tour; *Chemistry of Materials* 23, 923 (2010).
3. "H<sub>2</sub> Storage in Microporous Carbons from PEEK Precursors", Thomas P. McNicholas, Anmiao Wang, Kevin O'Neill, Robert J. Anderson, Nicholas P. Stadie, Alfred Kleinhammes, Philip Parilla, Lin Simpson, Channing C. Ahn, Yanqin Wang, Yue Wu, and Jie Liu, *Journal of Physical Chemistry C*, 2010, 114 (32), pp 13902–13908.
4. 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 (2010).
5. Symmetry-assisted hydrogen adsorption and control on transition metal incorporated porphyrins, Y-H Kim, Y.Y. Sun, W. I. Choi, J. Kang, and S. B. Zhang, *Phys. Rev. Lett.* under review (2010).
6. Hole mediated diffusion of H on sp<sup>2</sup> carbon networks, D. West, K. Lee, & S.B. Zhang, *Phys. Rev. Lett.* 104, 236101 (2010).
7. Theory of hydrogen Storage in nanoscale materials, Zhao, Kim, Zhang, Heben, in *The Oxford Handbook of Nanoscience and Technology, Frontiers and Advances*, Vol. 3, pp 700-736 (Oxford University Press, 2010)
8. Prediction of diamond-like, metallic boron structures, Yufeng Zhao, Qiang Xu, Lin J. Simpson, Anne C. Dillon; *Chemical Physics Letters* 496 (2010) 280–283.
9. "Hydrogen Sorption Center of Excellence Final Report", Department of Energy Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program, Lin Simpson, Director (2010).
10. Overview of the Hydrogen Storage Center of Excellence, as part of the DOE Annual Hydrogen Program Report (2010).
11. NREL Research as Part of the Hydrogen Sorption Center of Excellence, as part of the DOE Annual Hydrogen Program Report (2010).
12. Rich Chemistry and Structure Rule of sp<sup>2</sup> and sp<sup>3</sup> Boron," Y. Zhao, L.J. Simpson and A.C. Dillon, submitted.
13. An Electrical Study on Primary Hydrogen Spillover From Nanocatalyst to Amorphous Carbon Support, C. Lin, Z. Yang, T. Xu, and Yufeng Zhao, submitted.
14. Structural stability & 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.*).
2. "Capacity, Reproducibility, and Kinetics of the Weak Chemisorptive (spillover) Hydrogen Sorption Process," Thomas Gennett, Philip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, Lin J. Simpson, 2011 Hydrogen Metal Systems Gordon Research Conference, July 2011, MA.
3. "Weak Chemisorption Validation," Thomas Gennett, Philip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, Lin J. Simpson, DOE Fuel Cell Technologies Annual Merit Review, May 2011.
4. "Inter-laboratory Comparison Results on Measuring High-Surface-Area Materials For Hydrogen Storage and Critical Calibration Issues", Phillip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, Lin J. Simpson, Thomas Gennett, Spring MRS 2011, San Francisco, CA.
5. "Sorbents for Hydrogen Storage," Lin Simpson, Thomas Gennett, Philip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, Fuel Cell and Hydrogen Energy Association Conference, Washington DC, February 15, 2011.
6. Weak Chemisorption Validation, IEA HIA Task 22 Meeting, Freemantle, Australia Thomas Gennett, January 18<sup>th</sup>, 2011.
7. "NREL Weak Chemisorption Validation to DOE Hydrogen Storage Tech Team," Thomas Gennett, Philip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, and Lin J. Simpson, November 18, 2010.
8. "Development of Heterogeneous Sorbents/Sorbent Isotherm Measurement Materials Exchange," L. J. Simpson, DOE LANL-AIST Hydrogen Workshop, August 17-20, 2010, San Francisco, CA.
9. "Fundamental Research Needed for H<sub>2</sub> Storage by Sorbents," Lin Simpson, DOE-NSF Workshop, Alexandria VA, June 7, 2010.
10. "Research Needs for Hydrogen Storage," Lin Simpson, BES-EERE Workshop, Washington DC, June 3, 2010.

#### Presentations

1. "High Surface Area Boron Doped Carbon with Slow Hydrogen Desorption Kinetics," J. Bult, J. Blackburn, J. Lee, K. O'Neill, C. Engtrakul, P. Parilla, L. Simpson, T. Gennett, 2011 Annual Meeting of the Materials Research Society, San Francisco, CA.
2. "Sorbents for Hydrogen Storage," L. J. Simpson, Thomas Gennett, Philip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, NHA, February 2011.
3. "Chemical Vapor Synthesis of Boron Doped Carbon for Hydrogen Storage," J. Bult, J. Blackburn, C. Engtrakul, T. Gennett, J. Barker, K. O'Neill, L. Simpson, 2010 Annual Meeting of the Materials Research Society, Boston, MA.
4. Justin Bult, Atomic Layer Deposition of Platinum onto Functionalized Aligned MWNTs, ECS-Oct. 2010, Las Vegas, NM.

#### Invited talks

1. "Overview of Hydrogen Sorbents," Lin Simpson, Thomas Gennett, Philip A. Parilla, Kevin O'Neill, Katherine E. Hurst, Jeffery L. Blackburn, Chaiwat Engtrakul, Justin Bult, 242nd ACS National Meeting, Denver, Colorado, August 28 – September 1, 2011.

5. “Room-temperature study of hydrogen adsorption on carbon-based nanomaterials using diffuse reflectance infrared spectroscopy,” 240<sup>th</sup> American Chemical Society National Meeting, Boston, Massachusetts, August, 2010.
6. “Optical spectroscopy investigations of carbon-based nanomaterials for fundamental energy sciences research,” 240<sup>th</sup> American Chemical Society National Meeting, Boston, Massachusetts, August, 2010.