

## IV.C.6 Weak Chemisorption Validation

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### Subcontractor:

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Project Start Date: October 1, 2011

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

- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### 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 targets:

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

The specific technical objectives include:

- Conduct and correlate high-pressure NMR spectroscopy results with NREL DRIFTS to determine the specific C-H interactions involved in weak chemisorption-based hydrogen storage material.
- Determine the upper limit of percent by weight hydrogen uptake due to spillover in an optimized substrate matrix.
- Incorporate atomic level metal, (possibilities include Fe, Zn, Al, Ti, Ni, Co, etc.) into two distinct covalent-organic framework (COF) structures with pore diameters that may range of 30-100 angstroms via modified atomic layer deposition. The validation of the extent of metal incorporation within the final materials' matrix will be characterized by the appropriate X-ray, neutron scattering, Brunauer-Emmett-Teller, and/or spectroscopic techniques.

### Overall Objectives

Evaluate the weak chemisorption/spillover process as a means to achieve DOE 2017 hydrogen storage goals.

### Fiscal Year (FY) 2013 Objectives

- Evaluate universal reproducibility of enhanced adsorption weak chemisorption/spillover effects.
- Determine type of interaction of the support with the spilt-over hydrogen via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and nuclear magnetic resonance (NMR).
- Determine the theoretical, idealized upper limit of gravimetric sorption capacity from hydrogen spillover onto a carbon substrate.
- Communicate validated results to the community at large.

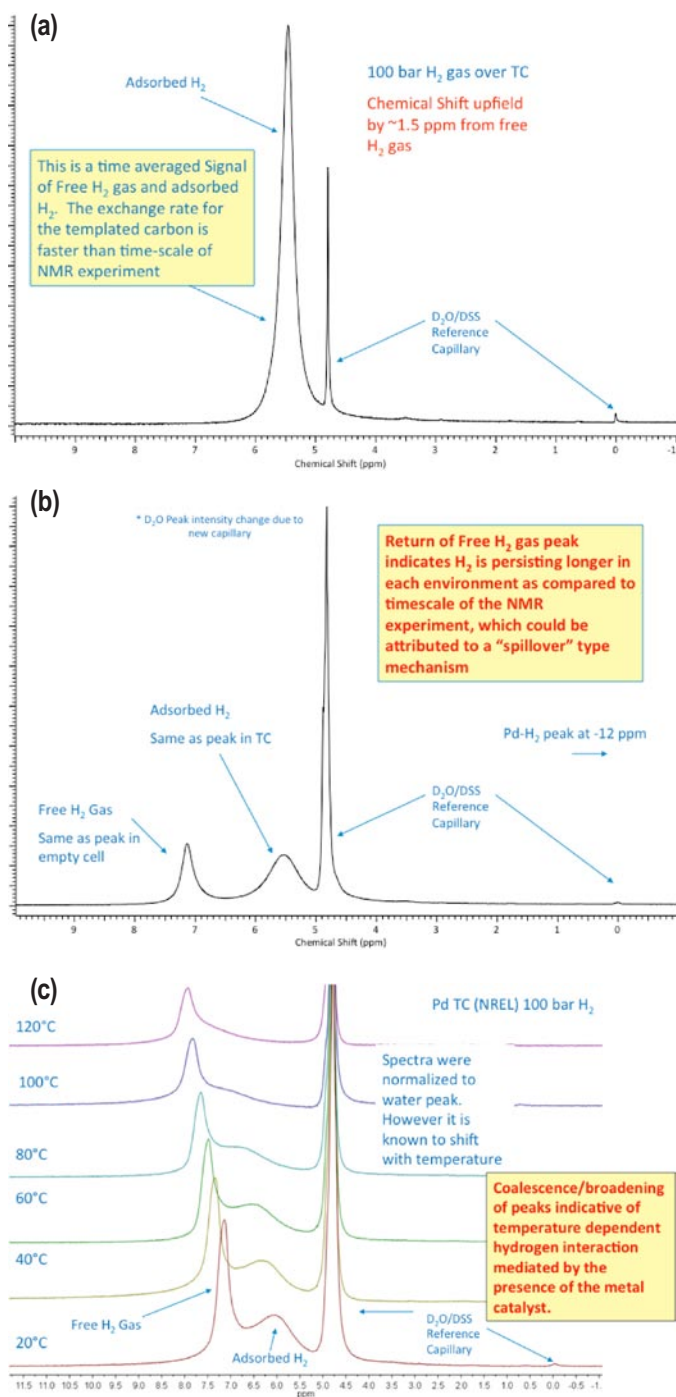
### Technical Barriers

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

- (A) System Weight and Volume

### FY 2013 Accomplishments

- We completed the initial series of variable temperature <sup>1</sup>H-NMR experiments on the templated carbon (TC) and palladium-decorated TC samples. The results are shown in Figure 1:
  - TC shows a single peak, so we are getting rapid exchange at the substrate surface on the timeframe of NMR and it is shifted upfield to approximately 5.6 ppm (Figure 1a).
  - For the Pd-TC carbon samples both the free H<sub>2</sub> (7.2 ppm) and carbon substrate (5.6 ppm) hydrogen gas peaks being present indicates H<sub>2</sub> is persisting longer in each environment, possible due to a stronger-spillover type interaction (Figure 1b).



**FIGURE 1.** <sup>1</sup>H NMR data of PdTC material that illustrates the appearance of a new C-H interaction upon exposure of the sample to hydrogen overpressures at room temperature.

- Coalescence of peaks indicates temperature dependence of the peaks and that the process is indeed a rapid exchange (Figure 1c).
- Demonstrated direct spectroscopic evidence of a reversible room temperature sorption/desorption apparently from a unique C-H interaction via DRIFTS and neutron scattering:

- DRIFTS measurements up to 100 bar hydrogen overpressure for Pd/TC showed a unique reversible infrared stretch that was tentatively assigned to spilt-over hydrogen (Figure 2).
- Series of X-ray raman experiments completed at Stanford National Accelerator Laboratory.
- Five articles published, three separate peer-review journal articles related to our efforts are in preparation.



## INTRODUCTION

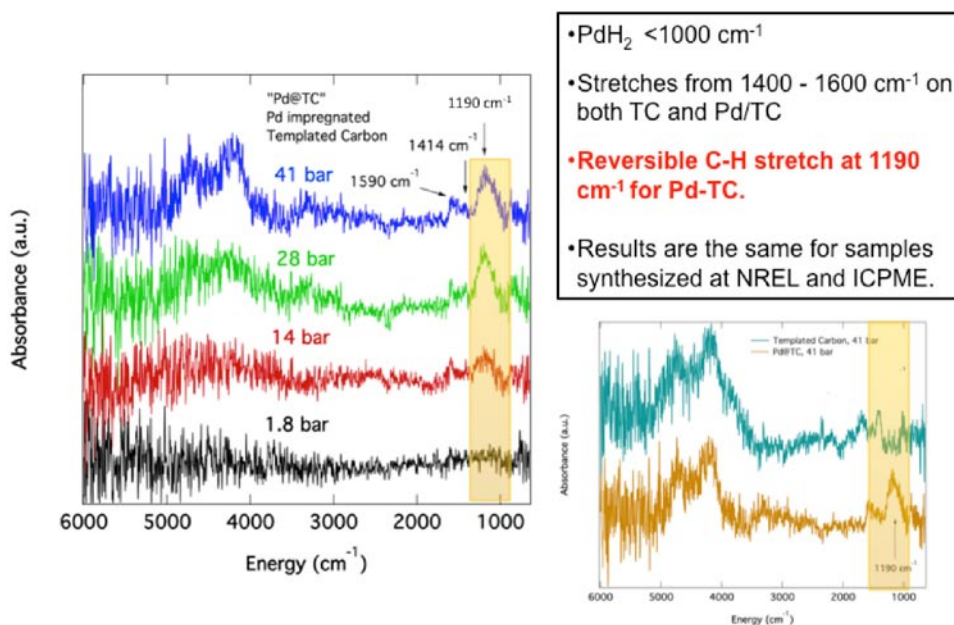
The ultimate goal of the Hydrogen Storage sub-program is the development of hydrogen storage systems that meet or exceed the DOE's goals for the onboard hydrogen storage in hydrogen-powered vehicles. With the tremendous interest in weak chemisorption materials for hydrogen storage, NREL and DOE have 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 H<sub>2</sub> storage mechanisms, so information gained on the hydrogen-substrate interactions should help accelerate viable sorbent development.

## APPROACH

Our approach included the synthesis and characterization of TC and Pd/TC materials with an unexplained enhancement of hydrogen sorption in the presence of catalysts that has been attributed in the past to hydrogen spillover. These materials were synthesized at NREL and through spectroscopic evaluation of the materials with DRIFTS and NMR we determined peak assignments in order to determine if spilt-over hydrogen spectroscopic modes are in regions expected for room temperature hydrogen desorption.

## RESULTS

1. **<sup>1</sup>H NMR evidence for spilt-over hydrogen on a Pd-TC material.** NREL synthesized multiple batch samples of Pd-TC for both DRIFTS and NMR experiments were performed. The results are shown in Figures 1 a-c.
2. **DRIFTS determination of new hydrogen-substrate interactions for an apparent spillover material.** Using infrared spectroscopy to identify distinct substrate-



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

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  $D_2$  and treated at various temperatures.

3. We completed the synchrotron spectroscopic investigation of hydrogen-matrix interactions on the sorbents.
4. Determined the upper limit of hydrogen uptake (weight percent) due to spillover in an optimized substrate matrix.

We performed, thorough density functional theory-based modeling of the whole process of hydrogen spillover in flat graphene sheets (2 nm by 3 nm) catalyzed by Pd particles (0.5 nm by 0.8 nm by 0.8 nm), addressing the issues of nucleation, growth patterns, and mechanism of H migration.

Our theoretical study revealed:

- The only sustainable hydrogen storage in graphitic material is through chemisorbed H pairs with the two H atoms bound to the adjacent C atoms in alternative sides of a graphene sheet.
- Nucleation of stable H chemisorptions starts with formation of compact, hexagonal H patches. The smallest stable patch contains 16 H atoms, with the average binding energy of 12 kJ/mol- $H_2$ . As the patch size increases, the binding energy increases and reaches to the maximum value of 40 kJ/mol at infinite size.
- Cooperative migration of the H pairs is required by the energetics and kinetically water can mediate the

cooperative migration by reducing the kinetic barrier to  $\sim 1.0$  eV. This indicates that moisture is important for improving kinetics of hydrogen spillover.

- Once the catalytic center is fully surrounded by chemisorbed H atoms, the H migration from the catalysts to carbon stops. This determines the maximum distance that H atoms can reach out from a catalytic center. If one assumes hexagonal patches, then ideally, six such patches with a size similar to the catalytic particle roughly fills the 360-degree angular space, which terminates the spillover around that catalytic particle. That gives a maximum area ratio of 6:1 of H covered graphene over that of metal-covered graphene. Based on this ratio and the lattice parameters and the standard atomic weight (12.011 for C, 106.45 for Pd), homogeneous distribution of Pd nanoparticles (3 atomic layer thickness, 2-nm diameter) on graphene, with optimum interdistance of 5-6 nm, the maximum H capacity is derived as  $2.75 \pm 0.25\%$  wt%.
- Stable topological defects (e.g. Stone-Walse defects) and boron dopants can improve both the kinetics and possibly the hydrogen capacity.
- 5. NREL will investigate application of “modified” atomic layer deposition techniques to incorporate various metal dopants into framework-type materials and the effect on the isosteric heat of adsorption for hydrogen.
  - COFs are porous materials in which organic building blocks are linked by covalent bonds. These crystalline extended structures exhibit high thermal stability and have pore sizes ranging

from 9-32 Å. A co-condensation reaction between 2,3,6,7,10,11-hexahydroxytriphenylene and 4,4'-biphenyldiboronic acid was utilized to produce COF-10 (32 Å). Reactions were carried out following a previously described method (see J. Am. Chem. Soc. 2007, 129, 12914-12915). In addition, COF-1 (15 Å) was produced using a simplified, one-step condensation reaction of 1,4-diboronic acid. The COFs above were produced in gram quantities allowing for more accurate analysis before and after metallation by atomic layer deposition. Atomic layer deposition experiments will proceed in the fourth quarter of FY 2013.

## CONCLUSIONS AND FUTURE DIRECTION

- Reconcile spillover propagation mechanisms:
  - Reconciled mechanism with metal-mediated processes and theoretically established maximum capacity for spilt-over hydrogen on a graphene surface.
  - Observed a reversible C-H interaction on Pd-TC via DRIFTS, NMR and neutron scattering.
- Determine ultimate spillover capacity possible with optimized interactions and substrate chemistry:
  - Theory predicts a “wet” gas composition to enhance diffusion (mediate) across substrate surface away from metal sites.
  - Determined a maximum hydrogen sorption for graphene at 2.75% w/w assuming both sides hydrogenated. For common carbon surfaces the capacity is expected to be much less.
- Stanford National Accelerator Laboratory Work:
  - X-ray raman spectroscopy technique should be able to detect hydrogen strongly bound to the carbon when the  $sp^2$  bonds are converted to  $sp^3$ .
  - We did not observe changes in the spectra that would support strong  $sp^3$  C-H bonding orbital which may be the result of:
    - We do not form a true  $sp^3$  for the C-H interaction did not occur for the Pd-TC material.
    - We may be below the detection limits because of the small number of C-H bonds formed are below the detection limits of the technique.
- Report detailing findings and recommendations at: Tech Team update, (September 2013); final analysis and recommendations were presented at the annual DOE Annual Merit Review, May 2013, and within a position paper submitted July 2013.

## FY 2013 PUBLICATIONS/PRESENTATIONS

### Publications

1. *Hydrogen adsorption properties of platinum decorated hierarchically structured templated carbons*, Hyunchul Oh, Thomas Gennett, Plamen Atanassov, Mert Kurttepel, Sara Bals, Katherine E. Hurst, Michael Hirscher, *Microporous and Mesoporous Materials* 177 (2013) 66–74.
2. *A Dynamic Calibration Technique for Temperature Programmed Desorption Spectroscopy*, K.E. Hurst, M.J. Heben, J.L. Blackburn, T. Gennett, A.C. Dillon and P.A. Parilla. *Review of Scientific Instruments* (2013) 84(2), 025103/1-025103/9.
3. *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, *J. Phys. Chem. C*, 2012, 116 (51), pp 26744–26755.
4. *Reactions and reversible hydrogenation of single-walled carbon nanotube anions*, C. Engtrakul, C.J. Curtis, L.M. Gedvilas, L.J. Simpson, P. A. Parilla, M. J. Heben, T. Gennett, *Journal of Materials Research* (2012), 27(21), 2806-2811.
5. *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, *J. Phys. Chem. C*, 2012, 116 (50), pp 26138–26143.
6. *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.
7. *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. NREL Hydrogen Storage Efforts-Task 32, Thomas Gennett (et.al) IEA-HIA Task 32 Kickoff meeting, Heraklion, Crete, Greece 21-25 April 2013.
2. Invited Talk; Weak hydrogen chemisorption validation, Thomas Gennett, DOE Fuel Cell Technologies Program Annual Merit Review, May, 2013, Washington, D.C.