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

A.C. Dillon (Primary Contact), J.L. Blackburn, C.J. Curtis, M. Davis, T. Elko-Hansen, C. Engtrakul, T. Gennett, M.J. Heben, K.M. Jones, Y-H. Kim, K.J. O'Neill, P.A. Parilla, J.D. Rocha, L.J. Simpson, E. Whitney, S.B. Zhang, Y. Zhao
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 384-6607; Fax: (303) 275-3109
E-mail: anne_dillon@nrel.gov

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

Subcontractors:
- Tom Gennette, Rochester, NY
- Shengbai Zhang, Troy, NY
- Karl Gross, Newark, CA

Project Start Date: February 1, 2005
Project End Date: The current materials CoEs are scheduled to end in Fiscal Year 2010.

Objectives

- Demonstrate a sorption system that meets the gravimetric and volumetric targets by developing a material that has an optimized binding energy, 15-20 kJ/mol such that non-sorbing system hardware will be kept to a minimum. (A balance-of-plant [BOP] has not yet been determined for sorption systems. However if binding energy is truly optimized, the BOP will be minimized.)
- Optimize refueling time by developing sorption materials that are not limited by heat transfer processes.
- 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.

Technical Barriers

This project addresses the following technical barriers from the on-board hydrogen storage technical barriers section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program 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

Hydrogen Sorption Storage Systems

This project is aimed at the development of high surface area hydrogen sorbents with dense volumetric packing. Importantly a system that contains hydrogen adsorption sites with an optimized binding energy (10-20 kJ/mol) are under investigation such that a system that operates at near ambient temperatures and pressures may be achieved. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: $4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L
- Charging/discharging rate: 3 min for a 5 kg system

Accomplishments

- Five classes of organo-metallic fullerene compounds have been synthesized and evaluated for hydrogen storage capabilities. Capacities range from 0.1-0.5 wt% at 77 K, 2 bar and 0.8-1.1 wt% at room temperature (RT) with no overpressure. The binding energies are ~4-6 kJ/mol and ~100 kJ/mol at 77 K and RT, respectively. Although theoretical molecules have not been achieved, significant insight into relevant chemical processes for hydrogen storage have been ascertained and employed in more tractable reactions.
- Theoretical calculations have been employed to probe a simple co-intercalation system with a capacity of 3.4 wt% for hydrogen with a binding energy in the range of 9-22 kJ/mol. Proof-of-concept synthesis was achieved in only two months.

This represents a significant step forward and a first time demonstration of the synthesis of a theoretically predicted system.

- Spillover materials similar to those fabricated at the University of Michigan have been synthesized at NREL. Confirmation of the spillover process on a Pt-activated high surface area carbon material has been achieved with a demonstrated twofold increase in RT capacity for the activated sample.
- Alternate spillover materials have also been explored at NREL. Na-reduced sp^2 hybridized carbons with approximately 2 wt% reversible storage at room temperature with no over pressure have been demonstrated.
- Tractable aromatic systems have been demonstrated as promising for their potential to stabilize di-hydrogen ligands on a first row transition metal atom.
- NREL has continued to develop and employ high-throughput measurement capabilities to accelerate discovery, development and partner interactions. For example new calibration methods have been developed that enable accurate high-pressure measurements with detection levels of ~40 µmoles.
- NREL has, to date, more than doubled the number of samples evaluated for others versus the number in Fiscal Year 2007 and continues to make measurements at this accelerated pace. Thus far a total of 69 samples have been thoroughly analyzed for partners/collaborators. Over 700 measurements were performed on external and internal samples.
- NREL has completed construction of a 1,500 ft^2 laboratory with improved gas phase synthesis capabilities that will allow for the incorporation of more reactive gases such that boron-doped materials may be readily made.
- NREL provided important scientific input for the initial sections of the "Best Practices" document including kinetics measurements as well as a general introduction and a preface section. These sections were posted for public comment on the DOE Web site in early May 2008.

✧ ✧ ✧ ✧ ✧

Introduction

NREL is leading the Hydrogen Sorption Center of Excellence (HSCoE) to develop reversible sorbent materials for hydrogen storage within the U.S. DOE National Hydrogen Storage Project. The HSCoE is developing the science base and technology advances required to meet DOE goals for on-board storage of hydrogen by researching a wide range of hydrogen sorbent materials. NREL performs research within the HSCoE on a variety of nanostructured and high surface area materials that may be comprised of carbon, metals, oxygen, and other elements. These materials show promise for break-through performance in vehicular hydrogen storage.

Approach

In order to accelerate progress in the focal areas that will result in the successful development of an onboard sorption system, NREL has organized its efforts into four research clusters (RCs). The same organization is also applied in the HSCoE as a whole. The research clusters are delineated below:

RC1: "Engineered Nanospace" Develop stable high surface area, minimally macroporous, light materials that can either stabilize large quantities of hydrogen directly (by physisorption), or provide frameworks for incorporating/stabilizing other species.

RC2: "Doped Materials" Increase concentration of substitutional dopants (e.g. B and N) in lattices to sorb dihydrogen directly (via donation), stabilize active species (e.g. transition metals) against agglomeration, or provide anchor points for building more complex sorbents.

RC3: "Strong Binding of H_2" Synthesize sorbents that can bind multiple dihydrogen ligands through metals that are capable of "Kubas" binding. Examples are chemical and gas phase syntheses of organo-metallic materials and metal organic frameworks (MOFs).

RC4: "Storage by Spillover" Develop methods to prepare catalytic species, bridges, receptors, and activation processes to reproducibly prepare spillover materials with high capacities and good kinetics.

All of the RCs require balancing hydrogen and material reactivity with the density and stability of the sorption sites. Furthermore the RCs build on each other: e.g. molecules developed in RC3 can be localized on doped (RC2) high surface area (RC1) materials. By promoting accelerated progress in each of these areas and then deploying the knowledge obtained in each RC for the fabrication of an optimized material, a system that meets the DOE on-board targets will be developed.

Results

Inspired by theoretical work of Zhao et al. [1] and Sun et al. [2], the organo-metallic chemistry of five fullerene-based systems has been explored. Table 1 shows a subset of findings from multiple experiments which were designed to make the target species including $Fe(C_{60})$, $Li(C_{60})$, $Fe(C_{60})$, $K(C_{60})$, and $Ca(C_{60})$. In Table 1, the synthesis of one representative compound is tabulated, but the detailed exploration of the numerous compounds probed for each system has been omitted for clarity. In order to demonstrate

the depth of analysis performed for each system, a detailed description of the $Ca(C_{60})$ system is provided here. The experimental synthesis of $Ca(C_{60})$ compounds was inspired by theoretical calculations indicating that $Ca_{32}C_{60}$ is capable of an uptake of ~8.4 wt% hydrogen, with a binding energy that may allow for near ambient adsorption [3].

TABLE 1. Subset of findings from multiple experiments designed to make target organo-metallic fullerene species.

Compound	Hydrogen Capacity	Binding Energy (kJ/mol)	Structure	Hydride Formation
$Fe(C_{60})$	0.5 wt%: 77 K, 2 bar 1 wt%: 77 K, 85 bar	6 kJ/mol	chain	no
$12Li(C_{60})$	0.8 wt%: RT, STP 0.2 wt%: 77 K, 2 bar	6 kJ/mol	polymer	LiH
K_6C_{60}	0.004 wt%: RT, 2 bar 0.06 wt%:77 K, 2 bar	N.A.	crystal	no
$32Ca(C_{60})$	1.04 wt% RT, STP 0.25 wt%: 77 K, 2 bar	>100 kJ/mol 4 kJ/mol	polymer	CaH_2
$Na(C_{60})$	1.1 wt% RT	~100 kJ/mol (onset)	ion	NaH

STP - standard temperature and pressure
N.A. - not available

The $Ca(C_{60})$ compounds were made by dissolving calcium in liquid ammonia with C_{60}. The ^{13}C solid-state nuclear magnetic resonance (NMR) spectrum of three different $Ca(C_{60})$ compounds is shown in Figure 1(a) where the number preceding the compound is the stoichiometric amount of calcium employed in each reaction for each C_{60} molecule. For the compound in which a large excess of Ca was employed, $57Ca(C_{60})$, it was not possible to detect the carbon features with ^{13}C solid-state NMR. In the spectra of the $10Ca(C_{60})$ and the $32Ca(C_{60})$ compounds, the broad features centered at ~144 ppm indicate that anionic C_{60} was formed. (A sharp feature at 143.7 ppm is characteristic of pure C_{60}.) The features at ~40 ppm indicate sp^3-hybridized carbon suggesting that C_{60} is polymerizing to some extent in both compounds. The fact that sharper features are observed for the $10Ca(C_{60})$ than for the $32Ca(C_{60})$ compound implies that a more ordered structure with specific binding sites for the Ca is observed. In all cases temperature-programmed desorption (TPD) measurements showed a moderately sized low-temperature hydrogen peak centered at ~100 K, consistent with physisorbed hydrogen. Also in all cases formation of the calcium hydride was observed resulting in capacities of ~0.8 wt% for each of the various $Ca(C_{60})$ species, with room temperature charging during synthesis. The desorption temperature of the calcium hydride is ~250°C as depicted in Figure 1(b) displaying TPD spectra of the $10Ca(C_{60})$ compound and CaH_2. (Similar TPD spectra were obtained for the $57Ca(C_{60})$ and $32Ca(C_{60})$ compound.) Volumetric measurements for the more ordered $10Ca(C_{60})$ compound yielded 0.17 hydrogen wt% at 77 K and 2 bar. For the $32Ca(C_{60})$ compound, the capacity increased to 0.25 wt% at 77 K and 2 bar. For the $57Ca(C_{60})$ compound, the capacity increased further to 1.30 wt% at 77 K and 2 bar. The C_{60} polymerization coupled with the CaH_2 hydride formation indicates that the theoretical compound was not formed explaining why the theoretical capacity was not achieved.

The theoretical high-capacity C_{60} structures have not yet been realized by wet chemical methods. However, C_{60} serves as a model system that is easy to characterize and the synthetic knowledge obtained from these studies

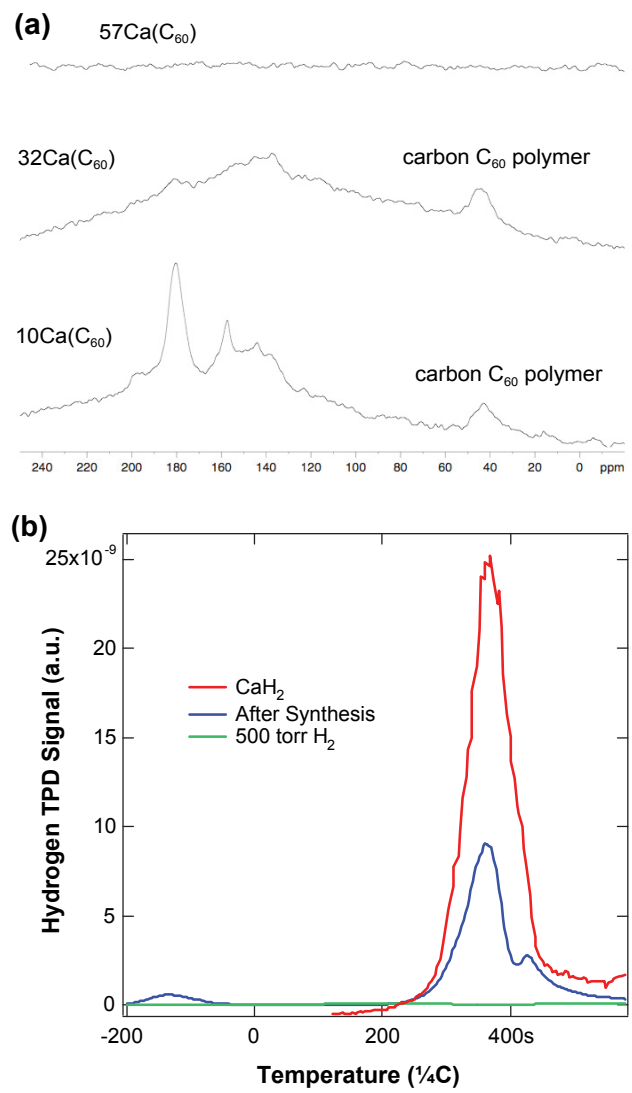

FIGURE 1. a) ^{13}C solid-state NMR spectrum of three different $Ca(C_{60})$ compounds where the number preceding the compound is the stoichiometric amount of calcium employed in each reaction and b) TPD spectra of the $10Ca(C_{60})$ compound and CaH_2.

has been transferred to simpler systems based on less expensive starting materials. The chemical synthesis of $CpScH_2(H_2)_4$ or similar compounds employing tractable reactions has begun. For example, the reaction path shown in Figure 2 was explored. However, it was not possible to isolate the Cl-bridged precursor shown in step 2 of the reaction. (NMR did not verify significant yield of the appropriate precursor.) Hence this reaction was not explored further, and a second reaction pathway shown in Figure 3 was developed to make a $C_9H_{13}ScH_2(H_2)_4$ compound. NMR spectra were obtained showing that the reaction products of step 1 and step 2 were isolated at high yield. The compound formed after step two was exposed to ~2 bar hydrogen in a sealed NMR tube. NMR spectroscopy indicated that the $CH_3C_6H_4NMe_2$ ligands were dislodged through the carbon linker suggesting that hydrogen is complexing with and/or dissociating on the Sc atom. However, hydrogen bound to the Sc was not detected in the NMR possibly because it was masked by the signal of the H_2 gas. Scale-up of the synthesis as well as other techniques to detect the hydrogen interacting with the Sc will be the subject of future work. This however may represent the synthesis of a compound with a dihydrogen ligand bound to a first row transition metal atom. Thus tractable reactions on simple aromatic systems have been shown promising for the development of on board hydrogen storage materials with moderate binding energies.

This year significant efforts to bridge the gap between theoretical predictions and experimental synthesis have been made. NREL worked to predict a simple system that not only had promising hydrogen storage properties but that could be easily synthesized. The theoreticians also performed calculations to aid in synthetic efforts. Figure 4 displays a graphical representation of a theoretically predicted co-intercalation graphite compound, where Li and tetrahydrofuran (THF) are the co-intercalation species forming $Li_4(THF)C_{72}$. Similar to the previously reported $Li_{12}C_{60}$ compound [2], the intercalated Li atoms serve to stabilize di-hydrogen species with binding energies that are enhanced relative to pure physisorption. The THF co-intercalant molecule plays two roles as it both prevents clustering and expands the graphite lattice to allow for H_2 adsorption. The $Li_4(THF)C_{72}$ co-intercalation compound has a reversible capacity of 3.4 wt% for H_2 coordinated with Li, resulting in enhanced binding energies in the range of 9~22 kJ/mol-H_2. The total hydrogen uptake capacity of the simple system is 5.7 wt%. This includes an additional 2.3 wt% physisorbed H_2 that is not interacting directly with the Li atoms and is adsorbed with a binding energy of ~5 kJ/mol-H_2. Calculations were also performed to determine the optimal amount of co-intercalation species. It was found that if the co-intercalation for Li exceeded a level of $Li_4(THF)C_{72}$, clustering of the Li and subsequent hydride formation was observed. The formation of the hydride is not desirable due to the increased binding energy as detailed in the previous discussion of the $Ca(C_{60})$ compound, where the CaH_2 species was observed to form. Finally, theoretical calculations were performed to examine other potential co-intercalation species. Figure 5 displays a graphical representation of benzene as co-intercalation species with Li (green balls) in graphite. For this system the benzene molecules are aligned in a planar fashion with the graphitic planes. The void space is then available for enhanced physisorption with a binding energy of ~9 kJ/mol-H_2. However, no H_2 binding to the Li atoms is observed as the Li orbitals are fully saturated by the graphene sheets and the benzene molecules. This

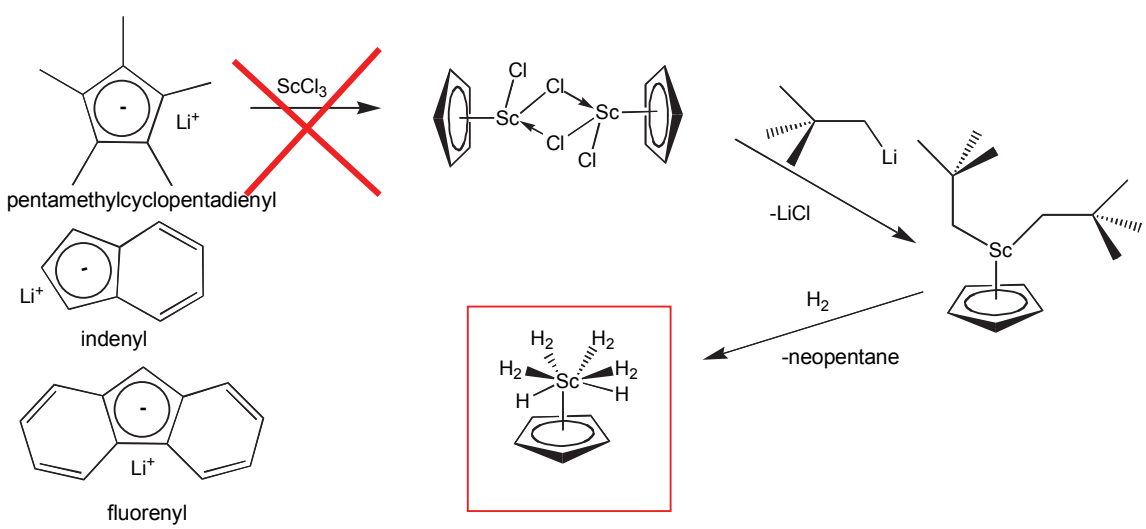

FIGURE 2. Reaction Pathway for the Wet Chemical Synthesis of $CpScH_2(H_2)_4$

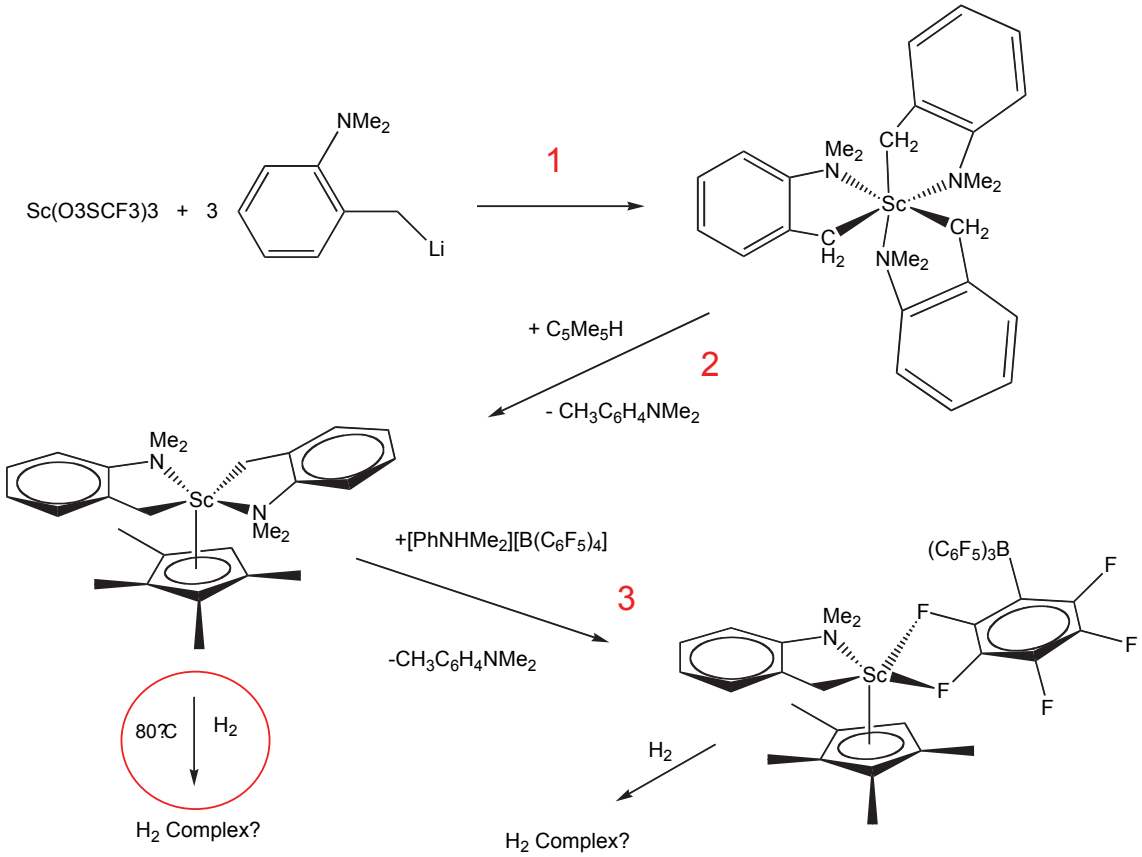

FIGURE 3. Reaction Pathway Developed to make a $C_9H_{13}ScH_2(H_2)_4$ Compound

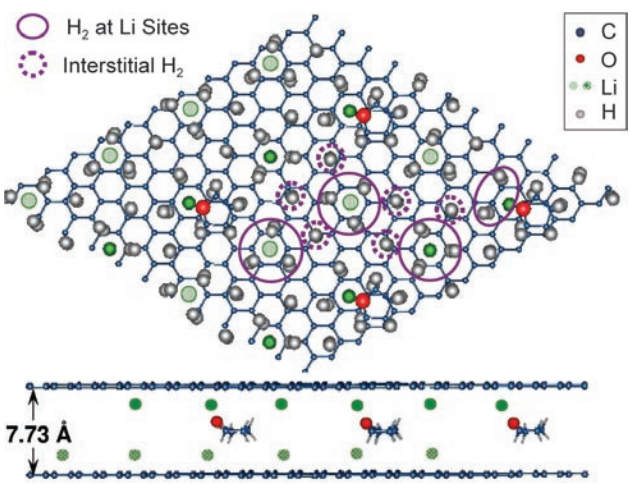

FIGURE 4. Theoretical representation of a co-intercalation graphite compound, where Li and THF are the co-intercalation species forming $Li_4(THF)C_{72}$.

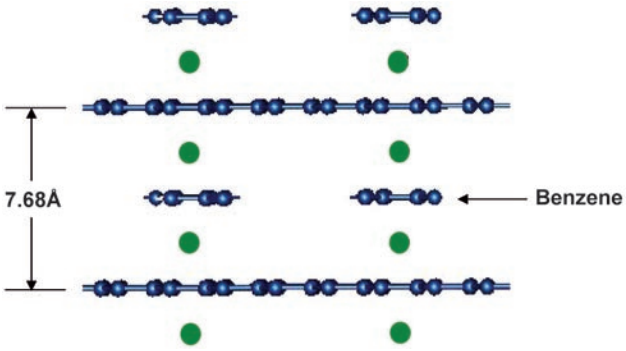

FIGURE 5. Theoretical representation of benzene and Li (green balls) as co-intercalation species in graphite.

saturation of the Li orbitals makes the Li-THF co-intercalation system preferable.

Demonstration of the synthesis of this Li-THF co-intercalation system was easily achieved in only two months by employing rapid, room temperature reactions to form the co-intercalation compounds. Briefly, the alkali metal naphthalide was reacted with graphite in THF. Temperature programmed desorption (TPD) was employed to confirm co-intercalation of THF. A dimethyltetrahydrofuran system was also explored for comparison, and it was found with TPD that only the Li intercalated (i.e. co-intercalation was not observed). The X-ray diffraction (XRD) spectrum in

Figure 6 shows that Li-THF co-intercalates into graphite to form stage 1 compounds. The formation of a stage 1 compound indicates that the intercalation species are present between each of the graphite layers. If a stage 2 compound were observed the intercalation species would be observed in every other layer of the graphite [4]. Volumetric studies were employed to examine the hydrogen adsorption properties of the Li-THF co-intercalated graphite, and the results were compared to the Li-intercalated graphite. The hydrogen adsorption capacities at both room temperature and 77 K, with an overpressure of 2 bar were obtained following no degas and degassing to 100°C and 250°C. The results are tabulated in Table 2. Under all conditions the Li-THF co-intercalated graphite was observed to adsorb more hydrogen than the Li-intercalated graphite. This confirms the theoretical prediction that the THF co-intercalation species is necessary to both prevent clustering and expand the graphite lattice allowing for H_2 adsorption. A maximum hydrogen capacity of 0.52 wt% was observed for the Li-THF co-intercalated graphite at 77 K, 2 bar following degassing to 250°C (Table 2). The XRD data in Figure 6 however reveals that a significant fraction of the graphite is not intercalated by the Li-THF co-intercalants. Future work will be devoted to increasing the yield of the intercalated graphite.

In FY 2008 NREL has also worked to reproduce the spillover results of Ralph Yang (University of Michigan) on Pt/activated carbon systems that were fabricated at NREL. NREL purchased CM-tec activated carbon and employed the method previously described by Yang to disperse Pt nanoparticles [5]. Briefly, H_2PtCl_6 in acetone is slowly added to an acetone solution containing the activated carbon. Several attempts were made until a uniform dispersion was achieved. Figure 7(a) displays a transmission electron microscopy (TEM) image of CM-tec activated carbon where a uniform dispersion of Pt nanoparticles was observed. Figure 7(b) displays the room temperature hydrogen adsorption isotherms for the CM-tec carbon and the Pt/CM-tec carbon with the results directly compared to the previously reported Yang results on AX-21 carbon and Pt/Ax-21 carbon [5]. For the AX-21 system approximately a five-fold increase in H_2 adsorption is observed at 800 torr on Pt/AX-21 compared to the control AX-21 carbon with the

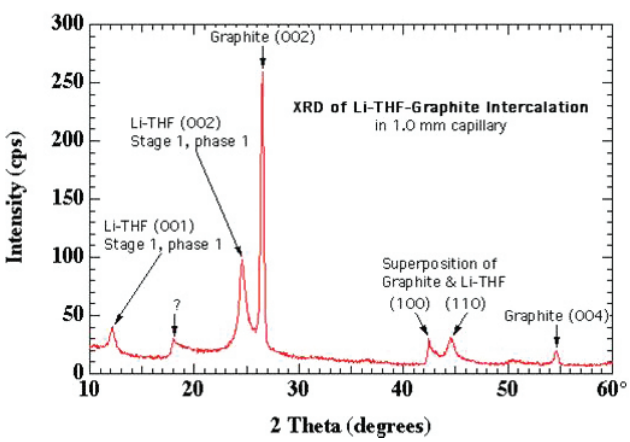

FIGURE 6. XRD Spectrum of Li-THF Co-Intercalation in Graphite

TABLE 2. Volumetric hydrogen adsorption capacities at 2 bar for both room temperature and 77 K, following no degas and degassing to 100°C and 250°C for Li-THF co-intercalated graphite and Li-intercalated graphite.

Sample	RT Degas		100 °C degas		250 °C degas	
2 bar volumetric	Wt% H_2 @ RT	Wt% H_2 @ 77 K	Wt% H_2 @ RT	Wt% H_2 @ 77 K	Wt% H_2 @ RT	Wt% H_2 @ 77 K
Li / THF	0.08	0.34	0.04	0.42	0.06	0.52
Li	0.003	0.02	Negligible	0.02	0.005	0.02

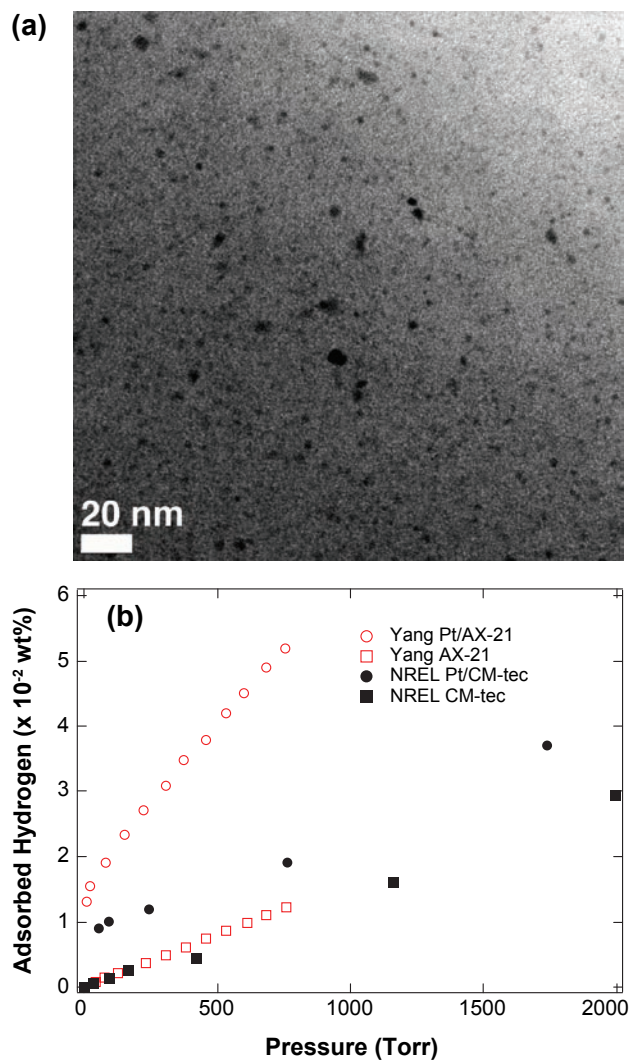

FIGURE 7. a) TEM image of CM-tec activated carbon with a uniform dispersion of Pt nanoparticles and b) room temperature hydrogen adsorption isotherms for CM-tec carbon and Pt/CM-tec carbon compared to previously reported results on AX-21 carbon and Pt/Ax-21 carbon.

enhanced adsorption attributed to the spillover effect. The Pt/CM-tec sample shows an approximate two-fold increase in H_2 adsorption at 800 torr compared to the CM-tec carbon also indicating spillover. The reduced spillover effect on the NREL sample may be attributed to the change in activated carbon or perhaps the Pt dispersion may still be improved. (CM-tec carbon was employed because AX-21 is no longer commercially available.) Thus the spillover process was confirmed at NREL. Future work will involve efforts to increase the capacity to comparable levels reported by Yang.

Significant research was also devoted to observing a spillover process on Na-reduced carbon single-wall nanotubes (SWNTs). The sodium-reduced nanotubes are synthesized by reaction with sodium naphthalide in THF. Subsequent infrared spectroscopy analyses indicate that the nanotubes are hydrogenated during synthesis. Synthesis in deuterated THF coupled with post mass spectrometry analyses confirmed that the THF was serving as the hydrogen source. In the infrared analyses the C-H stretching vibrations indicate that ortho-hydrogenation is observed as depicted in Figure 8(a). TPD studies of the NaSWNTs directly following synthesis reveal ~4 wt% hydrogen desorption between 473-773 K, corresponding to the complete formation of the ortho-hydrogenated species. The TPD spectrum of the NaSWNT sample directly following synthesis is shown in Figure 8(b). The high temperature hydrogen desorption is not reversible upon subsequent exposure to hydrogen gas. However a Pt catalyst was incorporated by mixing a small amount of Pt/CM-tec carbon (synthesis described above) with the NaSWNTs. Upon incorporation of the Pt catalyst, approximately 2 wt% hydrogen could be recovered reversibly following a room temperature hydrogen exposure. As shown in Figure 8(b) the hydrogen desorption from the Pt/NaSWNT sample is peaked at ~250°C. Future efforts will be focused on lowering the desorption temperature by introducing strain/dopants as well as on demonstrating this effect on inexpensive sp^2 hybridized carbon materials.

In FY 2008 the measurements team demonstrated an accelerated effort in order to keep pace with increased HSCoE synthesis productivity. Thus far a total of 69 samples have been thoroughly analyzed for partners/collaborators. This already more than doubles the number of samples evaluated for others in FY 2007. Furthermore over 700 measurements have been performed on external and internal samples. Measurement capabilities available to partners and other collaborators include: N_2 and H_2 Brunauer-Emmett-Teller surface area analyses, low- and high-pressure Sieverts (volumetric) measurements and TPD spectroscopy. All the necessary equipment and transfer procedures to allow for airless sample transport from external laboratories are in place. NREL also continues to improve its measurement capabilities. A

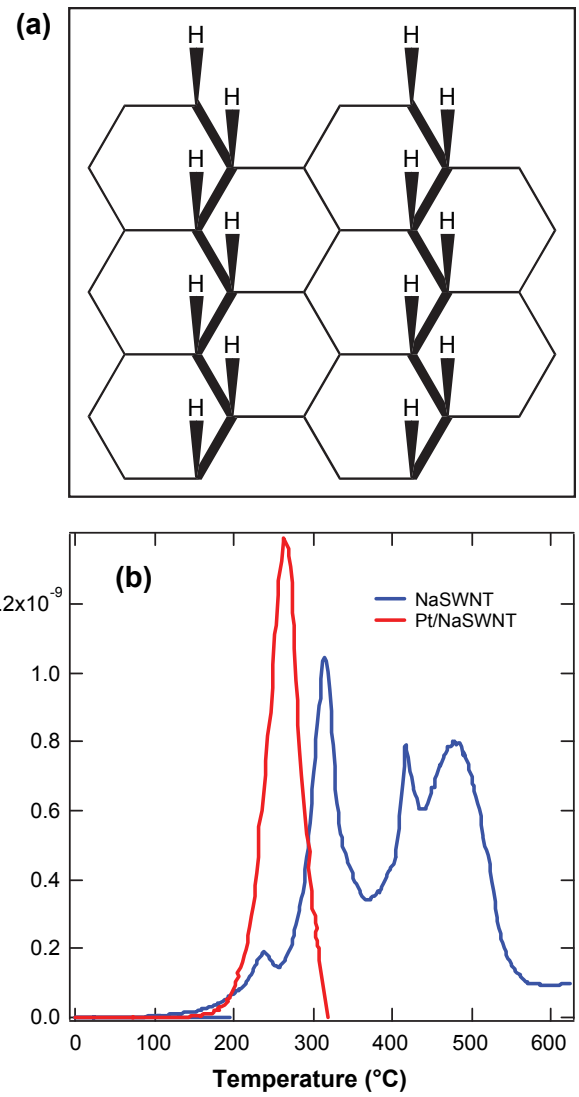

FIGURE 8. a) representation of ortho-hydrogenation of sp^2 hybridized carbon and b) hydrogen TPD spectra of NaSWNT's and NaSWNT's decorated with Pt.

new calibration method has been developed to enable accurate high-pressure measurements on small samples. With the new method, null adsorption experiments are performed in order to obtain the best headspace estimate. Multiple adsorption/desorption cycles are performed to show the error signal. The average of the step-by-step volume calculation allows for a robust estimate of the headspace volume. Detection at levels of ~40 µmoles H_2 may then be achieved.

According to theoretical calculations [1] the concentration of substitutional dopants such as boron must be increased substantially in order to either adsorb dihydrogen directly (via donation) or stabilize active species (e.g. transition metals) against agglomeration. Boron doping was previously demonstrated via laser vaporization of a graphite target doped with NiB in an

N_2 ambient. However the doping level of the boron was never observed to exceed 1-2 at% [6]. In order to achieve the optimized predicted hydrogen storage properties boron doping levels must reach close to 17% [1]. To demonstrate this increased doping level, it is believed that more reactive and consequently toxic gases must be employed. NREL has therefore completed fabrication of a new 1,500 ft^2 laboratory with laser vaporization arc-discharge and chemical vapor depositon techniques. The footprint of the laboratory is shown in Figure 9. The installation of toxic gas capabilities will be completed shortly. It will then be possible to utilize corrosive and toxic gases such as boron trichloride or diborane during synthesis. It is anticipated that increased boron loading will be observed as a result of incorporating reactive gases into the various gas phase processes.

Finally, there is a need to have common metrics and best practices for measuring the practical hydrogen storage properties of new materials that are being developed within the U.S. DOE Hydrogen Storage Program as well as at an international level. NREL therefore works with Karl Gross as the principle investigator (PI) through a subcontract to H_2 Technology Consulting LLC to develop a "Best Practices" document. This will provide a valuable resource to improve the accuracy and efficiency of performance measurements and to aid the entire program to achieve or exceed the technical storage targets. This project uses a combined approach of documenting the measurement experience of the PI and other experts in the field, reviewing and incorporating examples from the literature, when necessary performing experimental measurements to demonstrate important issues, and finally, condensing key information into a concise reference guide.

In FY 2008 the focus was on creating a best practices document for kinetics measurements as well as a general introduction and a preface section. Highly productive collaborations were established with Professor Sam Mao and Russell Carrington of the University of California, Berkeley. Dr. Gary Sandrock and Dr. George Thomas, consultants to the U.S. Department of Energy, Dr. Michael Miller of Southwest Research Institute in San Antonio, TX, Dr. Anne Dailly, Dr. Eric Poirier, and Dr. Frederick Pinkerton of General Motors Research and Development Center, Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller, Norway, Professor Channing Ahn of the California Institute of Technology in Pasadena, CA, Professor Sam Mao of the University of California, Berkeley in Berkeley, CA, and Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi of the National Institute of Advanced Industrial Science and Technology in Osaka, Japan. All provided valuable review and editing assistance, as well as, content for this initial document. Contributor's edits and comments were integrated into the final rough draft of the preface, introduction and kinetics documents. The preface section includes a foreword and terminology used throughout the Best Practices document. The introduction section includes an overview of hydrogen storage materials and the common techniques used to characterize the storage properties of such materials. The kinetics section covers such topics as the overall purpose of kinetics measurements, some basic theory, experimental consideration depending on the purpose of the

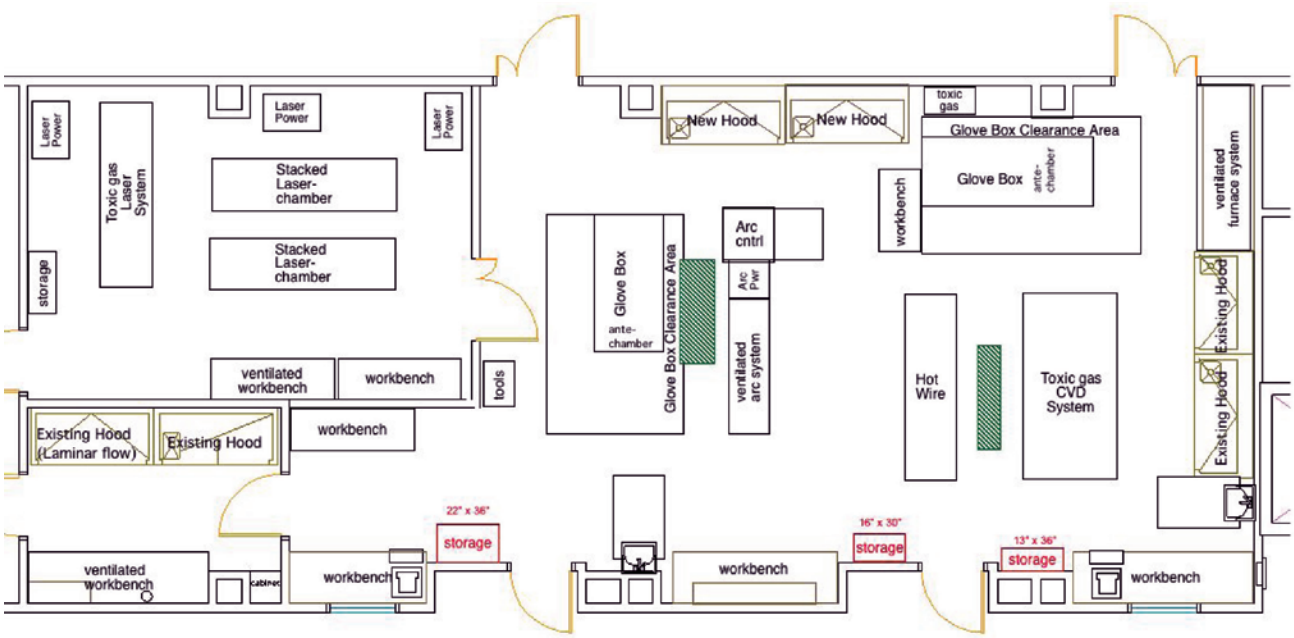

FIGURE 9. Footprint of the New Gas Phase Synthesis Laboratory

measurements, methods of measurement, and many details on both material properties and experimental factors that may strongly influence the final results and conclusions. This set of sections was submitted to NREL and the DOE for review and was posted for public comment on the DOE Web site in early May 2008.

Conclusions

- Multiple organo-metallic fullerene compounds have been evaluated for hydrogen storage capabilities. Significant insight into relevant chemical processes for hydrogen storage has been ascertained.
- Theoretical calculations have been employed to probe a viable co-intercalation system for hydrogen storage that may be easily synthesized, and proof of concept synthesis was achieved in only two months.
- Spillover materials similar to those fabricated at University of Michigan have been synthesized at NREL and the spillover process has been observed on the NREL generated materials.
- Alternate spillover materials, Na-reduced carbons, have also been explored at NREL. The Na-reduced carbons may be charged to ~2 wt% hydrogen reversibly at room temperature.
- Tractable aromatic systems appear promising for their potential to stabilize di-hydrogen ligands on first row transition metal atoms.
- NREL has continued to develop and employ high-throughput measurement capabilities to accelerate discovery, development and partner interactions.
- Improved gas phase synthesis capabilities such that boron-doped materials may be readily made are in place.
- A best practices document for kinetics measurements as well as a general introduction and a preface section was posted for public comment on the DOE Web site in May 2008.

Future Work

FY 2008

- Demonstrate dihydrogen ligand stabilization employing tractable reactions and determine optimized reaction pathway.
- Improve synthesis of co-intercalation compounds such that theoretical compound I obtained at high yield.
- Reduce reversible desorption temperature for Na-reduced carbons by incorporating strain or dopants into the carbon matrix.
- Continue to both verify University of Michigan spillover and develop new spillover processes.
- Employ reactive gases to increase boron loading in carbon materials.
- Calculate hydrogenation of metal intercalated graphite (another simple system) and continue to employ theoretical calculations to assist other synthetic efforts.
- Continue to develop state-of-the-art measurement techniques and to provide high-throughput measurement for partners.

FY 2009

- Employ successful organo-metallic reactions to high surface-area substrates obtained from center partners such as functionalized aerogels (Lawrence Livermore National Laboratory), MOFs (Texas A&M), carbon nanohorns (Oak Ridge National Laboratory) or nanotube scaffolds (Rice) to achieve high surface area sorbents with the maximum number of sites with moderate binding energies.
- Perform gas phase synthesis of targeted carbon and non-carbon sorbents. Specifically focus efforts such that theoretical doping levels for optimized storage will be achieved.
- Employ theoretical efforts that directly support the development of potential materials. In this way efforts targeted at synthesis will be accelerated.
- Work collaboratively with both Michigan and other groups exploring spillover such that this promising process is optimized.
- Determine optimal high-surface area system for organo-metallic chemistry, intercalation and/or spillover by working in conjunction with partners. These efforts will lead to the delivery of the most promising sorption material.
- Scale-up synthesis of most promising materials such that round-robin verification of samples and external validation may both be achieved.

Special Recognitions & Awards/Patents Issued

1. "Metal-doped single-walled carbon nanotubes and production thereof," A.C. Dillon, M.J. Heben, T. Gennett, P.A. Parilla, PCT Patent WO03/085178.

FY 2008 Publications

1. "Opening Space for H_2 Storage: Cointercalation of Graphite with Metal and Small Organic Molecules" Y. Zhao, Y-H. Kim, L.J. Simpson, A.C. Dillon, S-H. Wei, and M.J. Heben (Submitted).

2. "Hydrogenation Mechanism for the Reaction of Single-Walled Carbon Nanotubes with Tetrahydrofuran," T. Gennett, C. Engtrakul, C. Curtis, J.E. Ellis, J. Blackburn, A.C. Dillon, L. Simpson, K. Jones, P. Parilla, M. Heben (Submitted).

3. "Can one confine hydrogen molecule denser than 70 g/L? Dihydrogen interaction with oxidized calcium and magnesium", Y.-H. Kim, Y.Y. Sun, and S.B. Zhang (Submitted).

4. "Synthesis of Novel Metal Coordinated Fullerenes for Vehicular Hydrogen Storage" E. Whitney, C. Engtrakul, C.J. Curtis, K.J. O'Neill, P.A. Parilla, L.J. Simpson, Y. Zhao, Y-H. Kim, S.B. Zhang, M.J. Heben and A.C. Dillon Proceedings for International Symposium on Materials Issues in a Hydrogen Economy (in press).

5. "Challenges of a Hydrogen Economy: A Novel Organometallic Fe-C60 Complex for Vehicular Hydrogen Storage" E. Whitney, C. Engtrakul, C.J. Curtis, K.J. O'Neill, P.A. Parilla, L.J. Simpson, Y. Zhao, Y-H. Kim, S.B. Zhang, M.J. Heben and A.C. Dillon Mat. Res. Soc. Proc. (in press).

6. "Theory of Hydrogen Storage in Nanoscale Materials," Y. Zhao, Y.-H. Kim and S.B. Zhang. Book chapter 24, in *FRONTIERS IN NANOSCIENCE AND NANOTECHNOLOGY,* Vol. 3.

7. "Structural and Magnetic Studies of Two-Dimensional Solvent-Free Manganese(II) Complexes Prepared Via Ligand Exchange Reaction Under Solvothermal Conditions", Shengming Liu, Marshall Bremer, John Lovaasen, Anthony N. Caruso, K. O'Neill, L. Simpson, P.A. Parilla, M.J. Heben, and D.L. Schulz, Inorganic Chemistry (2008).

8. "Boron-Based Organometallic Nanostructure: hydrogen-storage properties and structure stability" Y. Zhao, M.T. Lusk, A.C. Dillon, M.J. Heben, S.B. Zhang, Nanoletters. *9*, 157-161 (2008).

9. "Effect of Spin State on the Dihydrogen Binding Strength to Transition Metal Centers in Metal-organic Frameworks", Y.Y. Sun, Y.-H. Kim, and S.B. Zhang, J. Am. Chem. Soc. 129, 12606 (2007).

10. "Novel Organometallic Fullerene Complexes for Vehicular Hydrogen Storage," A.C. Dillon, E. Whitney, C. Engtrakul, C.J. Curtis, K.J. O'Neill, P.A. Parilla, L.J. Simpson, M.J. Heben, Y. Zhao, Y-H. Kim and S.B. Zhang, *Physica Status Solidi (b)* 244 (2007) 4319-4322.

11. "Nontrivial Tuning of Hydrogen Binding Energy to Fullerenes with Endohedral Metal Dopants" Y. Zhao, M.J. Heben, A.C. Dillon, L.J. Simpson, J.L. Blackburn, H.C. Dorn, S.B. Zhang, *J. Phys. Chem. C.*, *111*, 13275 (2007).

FY 2008 Presentations

1. "Progress Towards Nano-Structured Hydrogen Adsorbants", P.A. Parilla (invited talk), Spring MRS 2008, San Francisco, CA, March 24-28, 2008.

2. "Weakly bound hydrogen interaction for onboard vehicle storage: From van der Waals to Kubas", Y.-H. Kim, Y.Y. Sun, Y. Zhao, K. Lee, and S.B. Zhang, (invited talksMaterials Research Society 2008 Spring Meeting, San Francisco, CA, Mar. 26, 2008.

3. "Hydrogen Sorption Materials Development," L. Simpson (invited talk) ACS Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, Febuary 24-27, 2008.

4. "Synthesis of Novel Metal Coordinated Fullerenes for Vehicular Hydrogen Storage," A. Dillon (invited talk) International Symposium on Materials Issues in a Hydrogen Economy" Nov. 12-15, 2007 Richmond, Virginia.

5. "A Novel Organometallic Fe-C60 Complex for Vehicular Hydrogen Storage" E. Whitney (invited talk) Challenges of a Hydrogen Economy: Fall Materials Research Society Meeting, Boston, Nov. 26-30, 2007.

6. "Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage," Yong-Hyun Kim, (invited talk) Michigan Technical University, Houghton, MI, October 15, 2007.

7. "First-principles study of nanostructured hydrogen absorbents for room-temperature reversible storage", S.B. Zhang, (invited talk) 3rd Annual Coordination Meeting of the DOE Computational Materials Science Network, Ames Laboratory & Iowa State University, Ames, IA, October 6, 2007.

8. "Synthesis of Novel Organometallic Fullerne Complexes for Vehicular Hydrogen Storage", A.C. Dillon, (invited talk) Materials Science & Technology Conference, Detroit, Sept. 16-20, 2007.

9. "First-Principles Study of Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage", S.B. Zhang, Y.-H. Kim, Y. Zhao, A. Williamson, Y. Sun, A.C. Dillon, M. J. Heben, (invited talk) AUTOMOTIVE: High-Density Hydrogen Storage for Automotive Applications: Materials and Methods" Materials Science and Technology Conference and Exhibition, Detroit, MI, 2007.

10. "Characterization of Nanomaterials to Optimize Renewable Energy Applications", A.C. Dillon, (plenary talk) NIST Workshop on Materials Characterization for Nanoscale Reliability, Boulder, Aug. 14, 2007.

11. "Synthesis of Novel Organometallic Fullerne Complexes for Vehicular Hydrogen Storage," A.C. Dillon, (invited talk) Materials Science & Technology Conference, Detroit, Sept. 16-20, 2007.

12. "DOE Carbon CoE Overview," M.J. Heben (invited talk) DOE Annual Merit Review, Alexandria, VA, May 15-18, 2007.

13. "NREL Reseearch as Part of the Carbon CoE," A.C. Dillon (invited talk) DOE Annual Merit Review, Alexandria, VA, May 15-18, 2007.

14. "DOE Carbon-based Hydrogen Storage CoE Overview," L.J. Simpson (invited poster) DOE Annual Merit Review, Alexandria, VA, May 15-18, 2007.

15. "Challenges of a Hydrogen Economy: A Novel Organometallic Fe-C60 Complex for Vehicular Hydrogen Storage" E. Whitney (contributed talk) Electrochemical Society Meeting, May, 2008, Phoenix, AZ.

16. "Mechanism of Hydrogen Storage on Reduced Carbon Single-Walled Nanotubes," C.J. Curtis, (contributed talk) Materials Research Society Spring Meeting, San Francisco, CA, March 26, 2008.

17. "Dihydrogen Binding in Metal-Organic Frameworks," Y.Y. Sun (contributed talk) Materials Research Society Spring Meeting, San Francisco, CA, March, 2008.

18. "Energetics of Hydrogen Spillover in Metal-Organic Frameworks," K. Lee (contributed talk) Materials Research Society Spring Meeting, San Francisco, CA, March, 2008.

19. "Hydrogen Storage in Novel Carbon-based Materials: Fe-C60," E. Whitney (contributed talk) International Symposium on Materials Issues in a Hydrogen Economy" Richmond, Virginia, Nov. 12-15, 2007.

20. "Hydrogenation Mechanism for the Reaction of Single-Walled Carbon Nanotubes Carbanions," T. Gennett, (contributed talk) Materials Research Society Meeting, Boston, MA, November 2007.

21. "Hydrogen Storage Materials Investigations of Nanostructured Sorbents," L.J. Simpson (contributed talk) Electrochemical Society Conference, Chicago, IL, May 5-11, 2007.

22. "Hydrogen Storage Materials Investigations of Nanostructured Sorbents," L.J. Simpson (contributed talk) Electrochemical Society Conference, Chicago, IL, May 5-11, 2007.

23. "Alkali Metal Reduced Carbon Single- Walled Nanotubes as Primary Hydrogen Storage Materials," T. Gennett, (contributed talk) Electrochemical Society International Meeting, Chicago, Illinois, May 5-11 2007.

References

1. Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, S.B. Zhang, *Phys. Rev. Lett.* **2005**, *94*, 155504.

2. Q. Sun, P. Jena, Q. Wnag, M. Marquez, *JACS* **2006**, *128*, 9741.

3. M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, Z. Zhang, *Phys. Rev. Lett.* **in press**.

4. H. Shioyama, *Syn. Met.* **2000**, *114*, 1.

5. Y. Li, R. T. Yang, *J. Phys. Chem. C* **2007**, *111*, 11086.

6. J. L. Blackburn, Y. Yan, C. Engtrakul, P.A. Parilla, K. Jones, T. Gennett, D.A.C., M.J. Heben, *Chem. Mater.* **2006**, *18*, 2558.