

IV.F.4 Hydrogen Fuel Cells and Storage Technology Project*

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Contract Number: DE-FG36-05GO85028

Subcontractors:

- The University of Nevada, Las Vegas (UNLV), Las Vegas, NV
- UTC Power, Inc, South Windsor, CT

Project Start Date: October 1, 2006

Project End Date: March 31, 2009

*Congressionally directed project

Technical Barriers

Storage barriers addressed by this project:

- (A) System Weight and Volume
- (D) Durability/Operability
- (P) Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Fuel Cell barriers addressed by this project:

- (A) Durability
- (B) Cost
- (C) Electrode Performance

Technical Targets

Technical Storage targets addressed by this project:

Gravimetric capacity, usable specific energy, volumetric capacity and durability/operability targets:

This project is conducting closely-coupled theoretical and experimental studies. The experimental effort enables rapid measurements of:

- Hydrogen adsorption/desorption in various pure and doped matrices.
- The electronic structure of metal and chemical hydrides.
- The electronic structure of C-B-N nanostructures with metal adatoms including effects of adsorbed hydrogen molecules and atoms.
- Synthesis and performance of mesoporous polymer/metal nanostructures.
- Synthesis and performance of sulfonated polyamide proton-exchange membranes for fuel cells:
 - Detailed electronic structure characterization for proton transport analysis.
- The theoretical effort is developing, validating and applying fundamental models and simulations of:
 - Electronic structure, bond character and strength, and the dynamics and kinetics of adsorption/desorption processes.
 - Structural effects of hydrogen adsorption/desorption in various nanomaterials.
 - Storage material properties and effects of temperature and pressure.
 - Ab initio molecular dynamics simulations to evaluate new proton exchange membrane (PEM) thermal and mechanical stabilities.

Objectives

- Perform closely-coupled theoretical and experimental investigations of:
 - Hydrogen adsorption/desorption in various matrices to establish a solid understanding of optimal storage concepts.
 - The electronic and geometric structure of metal hydrides, nanomaterials (C, B, N, transition metals, alloys), metal adatoms, and adsorbed hydrogen molecules/atoms.
 - Fuel cell membranes and catalytic materials.
- Predict optimized materials and structures for hydrogen storage and fuel cells in the DOE Hydrogen Program.
- Collaborate closely with external partners.

Accomplishments

- A graphenic C_3N_4 structure as an excellent template for alkali and 3-dimensional (3-D) transition-metal decoration which, in turn, can serve as high-capacity hydrogen storage media with the binding energies in a range (a few tenth of an electron volt) satisfying the fast kinetics required for mobile applications.
- A new computational approach for calculation of X-ray absorption spectroscopy (XAS) has been identified and code development is proceeding.
- The chemisorption energy per hydrogen atom decreases from about 2.0 eV for $Ti_{15}H_{20}$ to about 1.2 eV for $Ti_{13}H_{30}$; modulation of chemisorption energy by hydrogen loading can be significant in storage and catalyst applications.
- A novel class of Li-decorated 3-D materials consisting of ultrasmall diameter single-walled carbon nanotubes (SWCNTs) covalently functionalized by organic ligands has been designed for potential hydrogen storage applications.
- Alloying can have significant and quantifiable effect on hydrogen binding; the average chemisorption energy of $Ti_7Al_6H_{30}$ is about 0.52 eV/ H_2 molecule compared to 1.5 eV/ H_2 molecule for the $Ti_{13}H_{30}$ cluster.
- A change of the C hybridization state (from sp^2 to sp^3) in SWCNTs is found after adsorption of hydrogen.
- Ten different mesoporous polymer/Pd materials have been prepared using either chemical or electrochemical synthetic methods.
- Treating Pd(II)/aniline (0 M acid) with reducing agent $NaBH_4$ results in significant increase in hydrogen sorption rate; results suggest that $NaBH_4$ reduction and doping lowers the kinetic barrier for hydrogen sorption.
- Hydrogen sorption was measured at 1.6 wt% for Pd(II)/aniline without acid at hydrogen pressure of 30 psi and at room temperature; it is anticipated that increased pressure and optimization will provide much higher values of hydrogen uptake.
- Synthesis of new sulfonated copolyamides and their membrane properties were investigated. Among membranes tested, oxygenated diamine (ODA)-SCPA-70 showed high proton conductivity (105 mS/cm) at 80°C, which was comparable to that of Nafion[®] (104 mS/cm).
- Density functional theory (DFT) calculations of Pt_4 and Pt_3Co clusters shows that chemisorption of H_2 , O_2 , and CO molecules is energetically more favorable on the Co-doped cluster for all three diatomic molecules studied.
- For Pt_3Co clusters: H_2 undergoes dissociative chemisorption on the tetrahedral clusters in both head on and side on approaches to Pt centers; O_2

dissociation occurs in three and four center coordinations; and CO prefers to adsorb on Pt or Co atop atoms.

- Fuel cell catalyst annealing capability has been installed to permit replication of annealing procedures done at UTC Power, and both UNLV and UTC catalysts using soft X-ray and ultraviolet (UV) spectroscopies at UNLV and at the Advanced Light Source.



Introduction

Since hydrogen storage capacity, number of reversible cycles, kinetics of hydrogen absorption/desorption and catalysis of hydrogen and oxygen dissociation are closely related to material microstructures, atomic, molecular and nanoscale materials studies are particularly important for hydrogen storage and for fuel cell applications. Recent studies of hydrogen adsorption mechanisms by physisorption and chemisorption have shown strong temperature dependence of physisorption in nanotubes with high adsorption at elevated temperatures, while other studies favor low temperatures. A transition from sp^2 to sp^3 bonds during chemisorption has been reported in nanotubes and theoretical work shows application of external pressure enhances the bonding characteristics. Study of kinetic inhibition of bonding is warranted in the search for better performing storage concepts.

Cost and durability of fuel cell systems are crucial factors in their affordability. Limits on operating temperature, loss of catalytic reactivity and degradation of proton exchange membranes are factors that affect system durability and contribute to operational costs. Better understanding of the physical and chemical nature of catalyst performance, characterization of oxidation and reduction processes on system surfaces and development of improved mechanical and thermal stability of high performance proton exchange membranes are essential to cost effective devices.

Approach

The long-term goal of this project is to develop and apply a science-based framework for determining the maximal achievable specific storage capacity of a variety of solid state materials and concepts and to apply the same framework to advanced fuel cell membranes and catalyst materials.

Theoretical projects are aimed at providing improved understanding of issues related to storage and retrieval of H_2 adsorbed on host matrices including carbon and boron nitride nanotubes. The experimental tasks focus on the preparation of materials for hydrogen

storage and permeation and on a detailed structural and spectroscopic analysis of nanomaterials for hydrogen storage under various external conditions (high pressure, vacuum, elevated temperatures).

Fuel cell research for more cost-effective system designs is focused on the reactivity and durability of nanoclusters of catalyst materials, theoretical and experimental characterization of electronic structure of underlying substrates in the presence of oxidation and reduction processes, and the development and characterization of an improved sulfonated polyamide PEM.

Results

Theoretical and Experimental Studies of Storage Materials

A graphenic C_3N_4 structure has been identified as a template for alkali and 3-D transition-metal decoration for high-capacity hydrogen storage with binding energies around a few tenths of an electron volt. The porous structure of graphenic C_3N_4 provides strong bonding with the metal atoms and inhibits clustering of the metal ad-atoms overcoming a major obstacle for metal-decorated hydrogen adsorption. The results of charge distribution and partial density of states studies provide useful insights for exploration of other systems of similar properties. For example, boron as an alternative to metal atoms is under investigation.

A new computational approach for first-principles calculations of XAS will permit direct comparison of theoretical results with experimental data. Recently, extraction of wave-functions from the output of first-principles calculations that correctly reproduces the density of states has been achieved. This is a key step toward the goal of computing XAS. The principles for implementing such calculations have been worked out so that code development and test calculations can proceed.

Study is continuing of novel class of Li-decorated 3-D materials consisting of ultrasmall diameter SWCNTs covalently functionalized by organic ligands as potential hydrogen storage media. DFT calculations were performed to determine the stable structures and properties of Li-decorated nanoframeworks consisting of (5,0) SWCNTs constrained by phenyl spacers.

Carr-Parrinello molecular dynamics showed thermodynamic stability up to 20 ps at 300 K and up to 2 ps at 600 K. Structural calculations showed, however, that the presence of spacers affects Li coverage of the tubes resulting in the loss of a small percentage of Li atoms possibly leading to decrease of gravimetry for this system. In addition, the strong reactivity of ultrasmall diameter SWCNTs with Li atoms on the surface causes some spacers to be disconnected from the tubes,

potentially compromising system stability. Calculations with larger diameter SWCNTs (similar to the systems developed by J. Tour at Rice) will be undertaken in order to reduce the reactivity of the tube and improve the overall chemical/mechanical stability of these frameworks (Figure 1).

Small Ti clusters were studied to understand their catalytic activity and hydrogen storage properties. The catalytic effect of Ti, was studied by extensive calculations of electronic structures of $Ti_{13}H_m$ clusters using DFT with the B3LYP exchange-correlation functional. Ti_{13} was chosen because both experimental and theoretical studies indicate that it is energetically the most stable Ti_n cluster for $n=2-22$ atoms. Calculations showed that $Ti_{13}H_{20}$ and $Ti_{13}H_{30}$ are both energetically stable. In these hydrogenated clusters, each of the adsorbed hydrogen atoms is bonded to multiple Ti atoms. In $Ti_{13}H_{20}$, each of the dissociated hydrogen

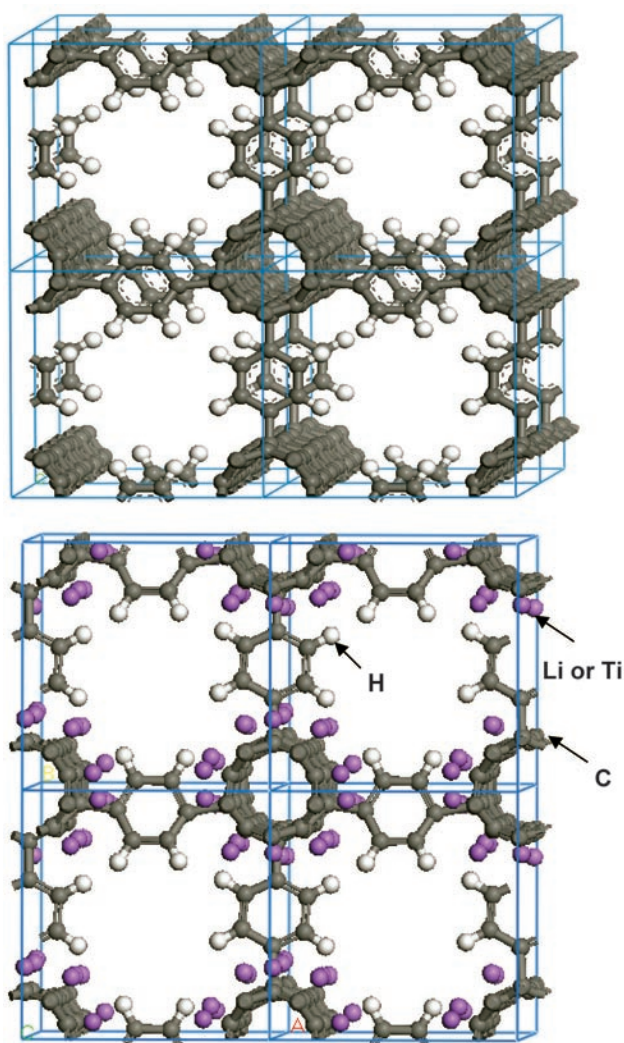


FIGURE 1. A Novel Class of 3-D Nanoframeworks based on CNTs Indicate that the Li-Decorated 3-D Nano-Frameworks are Promising for Hydrogen Storage

atoms is bonded to three Ti atoms leading to a three-center (μ_3) bonding. Further hydrogenation leads to a transition from three-center to two-center (μ_2) bonding. All of the hydrogen atoms in $\text{Ti}_{13}\text{H}_{30}$ are characterized by μ_2 bonding in which the hydrogen atom forms a bridge bond between two Ti atoms. The two types of bonding in $\text{Ti}_{13}\text{H}_{20}$ and $\text{Ti}_{13}\text{H}_{30}$ are illustrated in Figure 2(a). The transition from $\mu_3 \rightarrow \mu_2$ changes the average chemisorption energy of dissociated hydrogen atoms as shown in Figure 2(b). The chemisorption energy per hydrogen atom decreases from about 2.0 eV for $\text{Ti}_{13}\text{H}_{20}$ to about 1.2 eV for $\text{Ti}_{13}\text{H}_{30}$. Hydrogen multicenter bonds are affected by increased hydrogen loading and may be important for both hydrogen storage and catalyst design.

Calculations of the effects of alloying show that the average chemisorption energy of $\text{Ti}_7\text{Al}_6\text{H}_{30}$ is about 0.52 eV/ H_2 molecule compared to 1.5 eV/ H_2 molecule for the $\text{Ti}_{15}\text{H}_{30}$ cluster.

Experimental study of the effects on electronic structure of hydrogenation of various substrates is proceeding with the completion of the characterization system and development and implementation of source that provides either molecular hydrogen or atomic hydrogen. Procedures have been developed that permit spectroscopic study of individual SWNT (with and without decoration) so that data can be attributed solely to properties of the target and not affected by adjacent

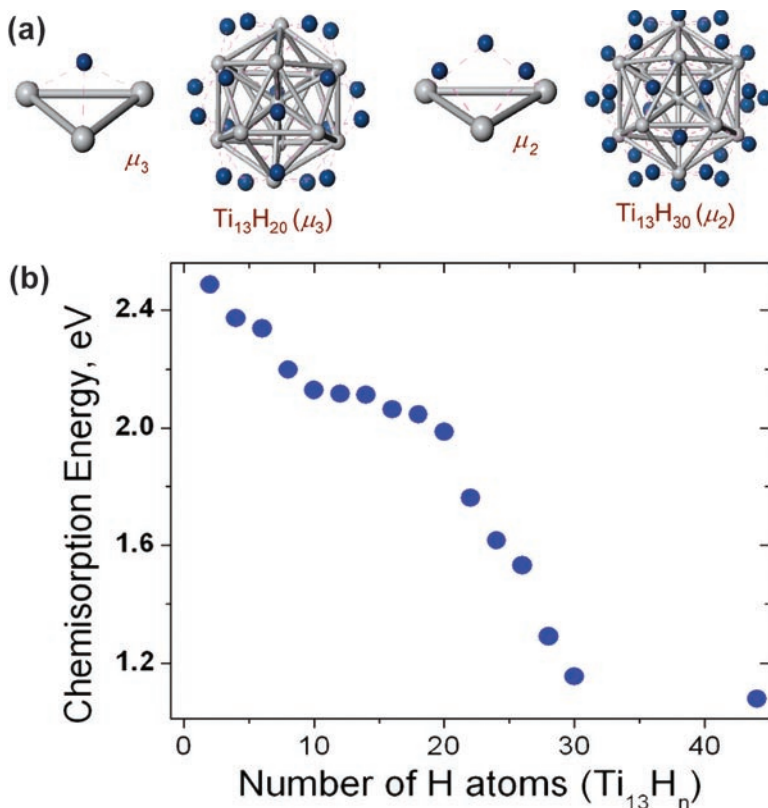


FIGURE 2. Hydrogen Multi-Center Bonds in Ti_{13}H_n ; μ_3 for $m \leq 20$ and μ_2 in $\text{Ti}_{13}\text{H}_{30}$

and contacting material. An example of this is shown in Figure 3 in which scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) methods were applied. To understand the effect of Ti decoration on the hydrogen sorption properties of carbon-based nanomaterials, such as SWCNTs and C_{60} , a series of experiments have been carried out, including hydrogenation of SWCNTs and C_{60} with and without Ti decoration. The C 1s spectrum for SWCNTs shows no difference before and after hydrogenation with molecular hydrogen, indicating that the chemical and electronic environment of carbon in SWCNTs is not affected by molecular hydrogenation. Hydrogenation with atomic hydrogen shifts the C 1s peak to higher binding energy, most likely due to a charge transfer between adsorbed atomic hydrogen and the C atoms of the SWCNTs. Valence band structures of SWCNTs also show changes as the hydrogenation shifts from molecular to atomic hydrogen. As the fraction of atomic hydrogen increases, there appears to be a transition of the C hybridization state (from sp^2 to sp^3) in SWCNTs. Meanwhile, the work function is also reduced as the atomic hydrogen fraction increases.

In order to understand how a sub-monolayer of Ti grows on SWCNTs, Ti was deposited on an Au-coated Si (Au/Si) substrate. It was found that Ti forms nano-clusters on the surface. Then, a sub-monolayer Ti

was deposited onto an Au/Si substrate pre-decorated with individual SWCNTs. One of STM images is shown in Figure 3. While individual bare SWCNTs can be imaged with atomic resolution (see also Figure 3), the adsorption of Ti leads to a “blurry” lateral corrugation of the surface electronic structure and hence no atomically resolved images of the Ti-decorated SWCNT have yet been obtained.

Synthesis and Characterization of Mesoporous Conductive Polymer/Pd

Conductive polymer/Pd structures have been prepared for evaluation of performance for on-board hydrogen storage and release. A total of eight different materials were synthesized chemically using PdCl_4^{2-} , PdCl_6^{2-} , aniline, and n-phenyl-phenylenediamine (NPPD). PdCl_4^{2-} produces a complex with aniline species and polymer with the analog containing two aniline units. NaBH_4 (applicable to all eight materials) was used to reduce the Pd to metal while reducing the polymer to increase the electron density. NaBH_4 also acts as a chemical dopant and may provide higher sorption of hydrogen based on known chemical

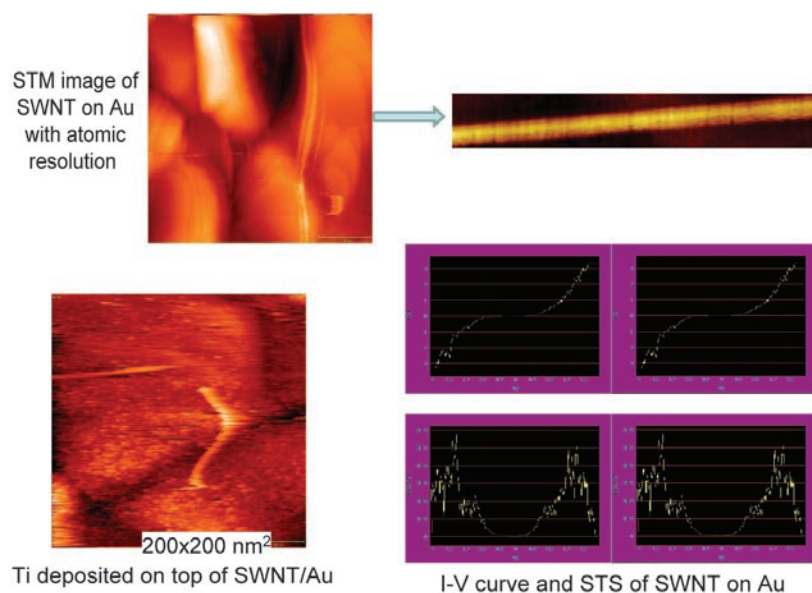


FIGURE 3. STM and STS Characterization of Individual SWCNT

pathways. However, reproducibility of results for NaBH_4 -doped PANI/Pd composites is unknown presently.

The percentage of Pd relative to the organic component was measured to determine if the Pd loading influences the hydrogen sorption for each material. The preliminary results indicate that two different materials are obtained with different Pd loading. The Pd(II) anion produced a complex rather than a polymer when reacted with aniline. However, polymeric material was obtained when Pd(II) was reacted with NPPD. Both the metal anion and the organic starting material influence the composite chemical structure during chemical synthesis. The percentage of Pd in the composite compared to the organic component is 26% and 10%, respectively, for aniline and NPPD composites. When the composites are exposed to a static pressure of 30 psi hydrogen for 40 minutes the percentage sorbed hydrogen is 1.60% for aniline/Pd(II). The value drops to 0.15% for the NPPD/Pd(II) material. The data indicates that a 62% reduction in Pd loading results in a 91% decrease in hydrogen sorption. The disproportionate decrease in hydrogen

sorption for Pd content indicates that the Pd content alone does not contribute the sorption properties.

The percentage of Pd in each material produced was obtained from thermal gravimetric analysis and is presented in Table 1.

Aniline monomer materials have a much higher Pd content. The question remains if the hydrogen sorption follows the same trends as the Pd loading. The results of the hydrogen sorption are presented in Table 2. It is clear from the table that not all samples with high Pd loading have favorable hydrogen storage properties. In fact for the material produced from the reaction of Pd(IV) with aniline in the absence of acid has a Pd loading of 26% with extremely low hydrogen sorption. In addition, with exception of Pd(II)/aniline with no acid,

materials produced with acid present showed a higher affinity for hydrogen and great storage.

The results in Table 2 suggest that whereas Pd loading affects hydrogen sorption, materials that have the same Pd loading do not provide the same degree of hydrogen sorption indicating the organic component also plays a role. The measurements are obtained at very low pressure 30 psi and room temperature. It is expected that higher loading pressures will result in higher sorption values. Therefore, additional pressure/sorption isotherm measurements are required to fully characterize the materials. In addition, sorption/time isotherms need to be measured to evaluate the kinetics of the sorption processes for each material. Finally, hydrogen sorption was measured for the Pd(II)/aniline (0 M acid) that was treated with reducing agent NaBH_4 (Table 3). The results are quite promising: measured hydrogen sorption and sorption rates increased. The results suggest that NaBH_4 reduction and doping lowers the kinetic barrier for hydrogen sorption to allow more rapid uptake.

TABLE 1. Pd Content in Percent from Thermogravimetric Analysis (TGA) Analysis

% Mass Loss (TG)

| | 0M PdII M | 1.0M PdII M | 0M PdIV M | 1.0M PdIV M | 0M PdII D | 1.0M PdII D | 0M PdIV D | 1.0M PdIV D |
|------------------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|
| | 71.75 | 72.88 | 73.59 | 70.99 | 88.81 | 79.21 | 91.02 | 84.54 |
| | 75.60 | 75.26 | 72.68 | 71.09 | 86.18 | 77.61 | 91.06 | 87.47 |
| 4th trial | 71.12 | 70.94 | 72.66 | 71.03 | 92.27 | 78.91 | 92.08 | 88.46 |
| | 78.15 | 73.70 | 75.79 | | 89.92 | 80.21 | 95.50 | 89.12 |
| Average | 74.16 | 73.20 | 73.68 | 71.04 | 89.30 | 78.99 | 92.42 | 87.40 |
| Standard Deviation | 3.32 | 1.80 | 1.47 | 0.05 | 2.53 | 1.07 | 2.11 | 2.02 |
| RSD | 4.48 | 2.46 | 2.00 | 0.07 | 2.83 | 1.36 | 2.29 | 2.31 |
| Pd content in % | 25.85 | 26.81 | 26.32 | 28.96 | 10.71 | 21.02 | 7.59 | 12.60 |

TABLE 2. Hydrogen Sorption Compared to Pd Content in Percent

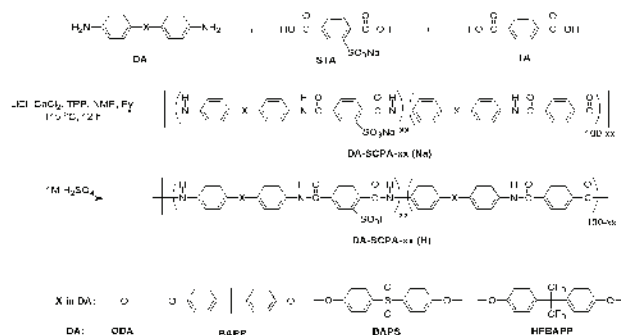
| % Hydrogen Time(minutes) | Pd II M OM A | Pd II M 1M A | Pd IV M OM A | Pd IV M 1M A | Pd II NPPD OM A | Pd II NPPD 1.0M A | Pd IV NPPD OM A | Pd IV NPPD 1.0M A |
|-----------------------------|--------------|--------------|--------------|--------------|-----------------|-------------------|-----------------|-------------------|
| 5 | 0.0888 | 0.0128 | 0.0147 | 0.0139 | 0.0387 | 0.1961 | 0.0056 | 0.0705 |
| 20 | 1.3051 | 0.8612 | 0.0052 | 0.0034 | 0.1203 | 0.3997 | 0.0413 | 0.1341 |
| 40 | 1.6010 | 1.0180 | 0.0019 | 0.7751 | 0.1689 | 0.5115 | 0.0905 | 0.1697 |
| Pd content in % | 25.8450 | 26.8050 | 26.3200 | 28.9633 | 10.7050 | 21.0150 | 7.5850 | 12.6025 |

TABLE 3. Hydrogen Sorption for Pd(II)/Aniline and Pd(II)/Aniline Treated with NaBH₄

| % Hydrogen Time(minutes) | Pd II M OM A | Pd II M OM A NaBH ₄ |
|-----------------------------|--------------|--------------------------------|
| 5 | 0.0888 | 1.811 |
| 20 | 1.3051 | 1.815 |
| 40 | 1.6010 | 1.817 |
| Pd content in % | 25.8450 | 25.8450 |

Synthesis and Characterization of Sulfonated Copolyamide Membranes

Polycondensation reactions of various diamines, terephthalic acid (TA), and sulfonated terephthalic acid (STA) produced high-molecular-weight sulfonated copolyamides:



By changing the ratio of TA and STA, sulfonated polymers with different degrees of sulfonation could be obtained. Based on intrinsic viscosity measurement, all sulfonated polymers were found to have high molecular weights (intrinsic viscosity >1.0 dL/g).

Thin film of DA-SCPA (Na) was prepared and conversion of the ionomers to SO₃H form was conducted in aqueous sulfuric acid solution. Membrane properties of DA-SCPA (H) were evaluated (Table 4). The experimental ionic exchange capacity (IEC) values measured from the titration agree well with the calculated ones of the theoretical polymer structures that were derived from the molar ratio of TA to STA. This result clearly indicates that the targeted polymer structures were successfully synthesized and all sodium sulfonate form of the sulfonated polymers was quantitatively converted to the corresponding sulfonic acid form. The sulfonic acid form membranes with

IEC = 1.00–1.80 mequiv/g show water uptake values in the range of 10–32 wt%, which are relatively lower than those of other hydrocarbon-based PEMs having similar IECs. To evaluate oxidative (chemical) stability in a condition similar to fuel cell environment, Fenton test was conducted by soaking the membranes in Fenton’s reagent (3% H₂O₂ containing 2 ppm of FeSO₄). Oxidative stability was evaluated by measuring the amount time for the membranes to become brittle (τ_1) and to start to dissolve into the reagent (τ_2).

TABLE 4. IEC, Water Uptake, Oxidative Stability of Sulfonated Aromatic Polyamides

| Sulfonated polyamides | IEC (mequiv/g) | | Water uptake (%) ^d | Oxidative stability ^e | |
|-----------------------|-------------------|--------------------|-------------------------------|----------------------------------|----------------|
| | expt ^a | calcd ^b | | τ_1 (min) | τ_2 (min) |
| ODA-SCPA-40 | 1.10 | 1.05 | 17 | 50 | 110 |
| ODA-SCPA-50 | 1.34 | 1.33 | 23 | 45 | 100 |
| ODA-SCPA-60 | 1.58 | 1.56 | 24 | 45 | 95 |
| ODA-SCPA-70 | 1.80 | 1.83 | 33 | 55 | 120 |
| BAPP-SCPA-70 | 1.17 | 1.06 | 17 | 65 | 150 |
| BAPS-SCPA-70 | 1.13 | 1.11 | 10 | 70 | 165 |
| HFBAPP-SCPA-70 | 0.99 | 0.94 | 13 | 135 | 260 |

^a Experimental ionic exchange capacity measured by titration.
^b Calculated ionic exchange capacity based on structures of sulfonated polyamides.
^c Calculated equivalent weight based on structures of sulfonated polyamides.
^d Water uptake (%) = $\frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$, where W_{dry} and W_{wet} are the weights of dried and wet membranes, respectively.
^e Oxidative stability measured by Fenton test where T_1 is the elapsed time for the membrane to start to become brittle and T_2 is the time for the membrane to start to dissolve in the solution.

Thermal stability of the sulfonated copolyamides in sulfonic acid form was measured with TGA in an inert gas atmosphere. The TGA curves of ODA containing polymers are shown in Figure 4(a). When compared with the thermal stability of non-sulfonated polyamide (ODA-SCPA-0 of Figure 4(a)), prepared from polycondensation reaction of TA and ODA, the incorporation of sulfonic acid groups into the polymer main chain induced decreased thermal stability of the sulfonated polymer. The first degradation step of the ODA-based sulfonated polymers was observed around 300°C because of the cleavage of C–S bond and the desulfonation of SO₃H. Among the series of ODA-based

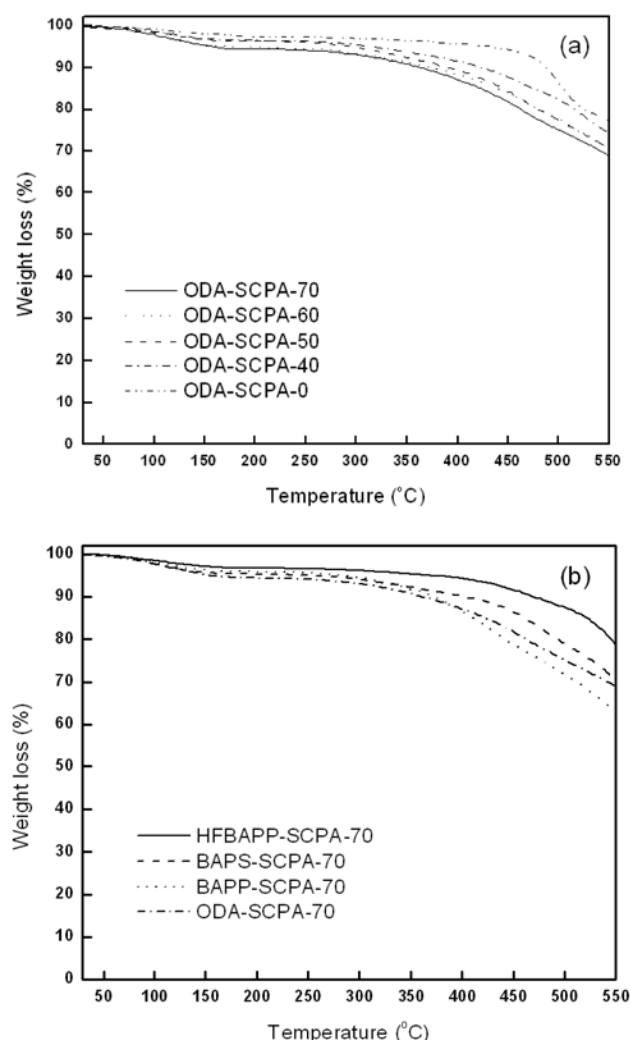


FIGURE 4. TGA Curves of (a) A Series of ODA-Based Sulfonated Copolyamides in their Acid Form and (b) A Series of 70% Sulfonated Copolyamides that were Prepared from Different Diamine Monomers

polymers, as the DS increases, the weight loss of the membrane resulting from the desulfonation increases (Figure 4 (a)). Thermal stabilities of DA-SCPAs derived from different diamine monomers were also studied. As shown in Figure 4(b), when the four different DA-SCPAs with the same 70% DS were examined, dependence of thermal stability on the diamine monomer structure was observed. Similar to the oxidative stability data, HFBAPP-SCPA-70 exhibited the lowest weight loss in TGA.

Proton conductivities of DA-SCPA (H) were measured at various temperatures under 100% relative humidity using a BektTech membrane proton conductivity measurement system (Figure 5). Among membranes tested, ODA-SCPA-70 showed high proton conductivity (105 mS/cm) at 80°C, which was comparable to that of Nafion® (104 mS/cm).

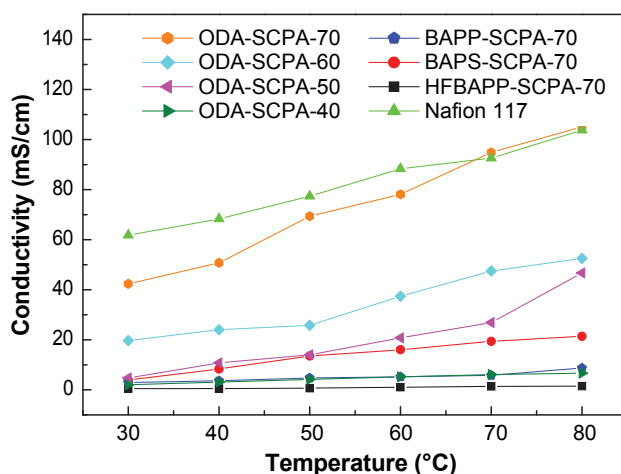


FIGURE 5. Proton Conductivity of Sulfonated Copolyamides at Different Temperatures under 100% Relative Humidity

Nanocatalysts and Clusters

We have investigated electronic structures of small clusters of Pt and looked into the growth of small Pt clusters on α -Al₂O₃ surface. Though electronic structures of subnanoclusters of Pt and Pd have been extensively investigated their interaction between support materials have not been well understood. A paper on the growth pathway of small Pt clusters on alpha-alumina is published in J. Phys. Chem.-C (2007).

Pt-Co bimetallic alloy has often been employed in polymer electrolyte membrane fuel cells. The structural and physicochemical properties of pure and Co-doped Pt clusters have been analyzed. It was found that chemisorption on the Co-doped cluster is energetically more favorable for all three diatomic molecules studied. This is explained in terms of charge transfer from Co to Pt leading to an increased *d*-orbital density of states for the doped cluster near the Fermi level compared to the pure Pt₄ cluster as illustrated in Figure 6.

Effective back bonding from the metal to adsorbed molecules occurs in both O₂ and CO adsorptions and the overlap is more favorable in Pt₃Co. While H₂ undergoes dissociative chemisorption on the tetrahedral clusters in both head on and side on approaches to Pt centers, O₂ dissociation occurs in three and four center coordinations and CO prefers to top-adsorb on Pt or Co. The tetrahedral structure becomes distorted as a result of H₂ and O₂ adsorption and tetrahedral Pt₃Co transforms to a planar rhombus structure after CO adsorption. Also, H₂ and O₂ adsorption at Co atop and Pt-Co bridge site lead to equivalent final geometries. This work is published in J. Chem. Phys. (2008).

A tube furnace and quartz tubes (under order) will allow duplication of the fuel cell catalyst annealing procedures performed at UTC. Pt-based fuel cell

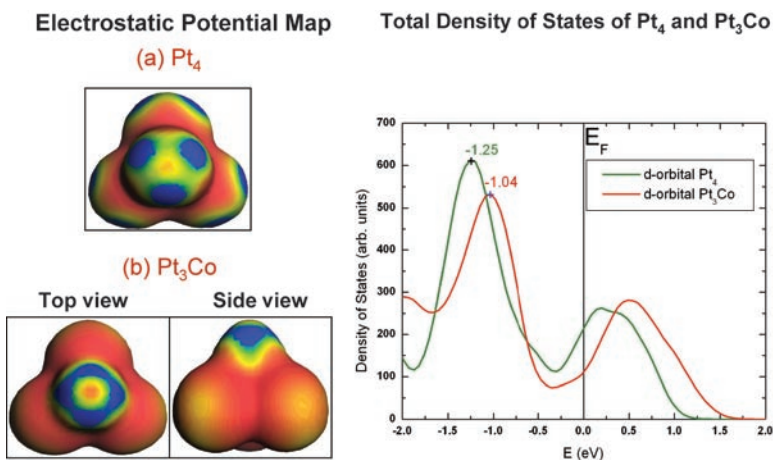


FIGURE 6. Position of the D-Band Relative to the Fermi-Level has Important Consequences to the Catalytic Activity

catalysts prepared at UTC and UNLV have been studied by using synchrotron- and lab-based soft X-ray and UV spectroscopies in order to understand their chemical properties, to investigate the presence (or absence) of a core-shell structure, and to gain insight into their electronic properties.

By comparing to reference samples (Figure 7(a)), Co in the catalysts transforms gradually from the Co-containing precursor into metallic Co. The influence of oxygen is more pronounced in samples that were treated at lower annealing temperatures. Co L-edge X-ray emission spectra (XES) from the same set of samples are shown in Figure 7(b). The decrease of spectral intensity on the left hand side of the main features (i.e., at lower photon energies) indicates that Co $3d$ occupied states follow a similar trend as the unoccupied states in the XAS spectra. The intensity ratio between the two main features (intensity at approximately 792 eV divided by intensity at approximately 777 eV) also gradually decreases with increasing annealing temperature. This is due to a self-absorption effect that can be used to monitor the density of Co near the emitting atom. Note that the observed ratio for the sample annealed at 925°C is still larger than that found for Co metal. This indicates that other atomic species (e.g., oxygen) are still present in the vicinity of the emitting Co atom.

Conclusions

Theoretical Studies and Electronic Structure of Storage Materials

- A graphenic C_3N_4 structure serves as a template for alkali and 3-D transition-metal decoration for H_2 storage with the binding energies around a few tenths of an electron volt.

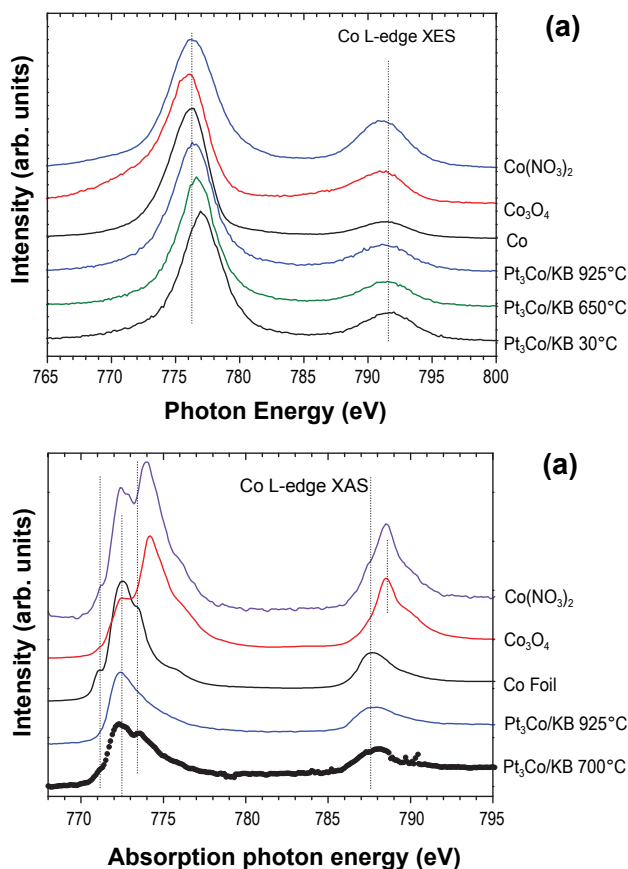


FIGURE 7. XES and XAS Characterization of Co Samples and Catalysts (a) Co L-Edge XES from Reference Samples and Catalysts (b) Co L-Edge XAS from Reference Samples and Catalysts

- A new computational approach for calculation of XAS is under development.

- Chemisorption energy per hydrogen atom decreases from about 2.0 eV for $Ti_{13}H_{20}$ to about 1.2 eV for $Ti_{13}H_{30}$.
- A Li-decorated 3-D framework of ultrasmall diameter SWCNTs covalently functionalized by organic ligands has been designed.
- The average chemisorption energy of $Ti_7Al_6H_{30}$ is about 0.52 eV/ H_2 molecule compared to 1.5 eV/ H_2 molecule for the $Ti_{13}H_{30}$ cluster.
- A change of the C hybridization state (from sp^2 to sp^3) in SWCNTs is found after adsorption of hydrogen.

Synthesis and Characterization of Mesoporous Conductive Polymer/Pd Concepts

- Ten different polymer/Pd materials have been prepared using either chemical or electrochemical synthetic methods.
- Treating Pd(II)/aniline (0 M acid) with reducing agent $NaBH_4$ results in significant increase in hydrogen sorption rate suggesting kinetic barrier reduction.
- Hydrogen sorption was measured at 1.6 wt% for Pd(II)/aniline without acid at hydrogen pressure of 30 psi and at room temperature; it is anticipated that increased pressure and optimization will provide much higher values of hydrogen uptake.

Synthesis and Characterization of New Sulfonated Copolyamide Membranes for Fuel Cell Applications

- Synthesis of new sulfonated copolyamides and their membrane properties were investigated. Among membranes tested, ODA-SCPA-70 showed high proton conductivity (105 mS/cm) at 80°C, which was comparable to that of Nafion® (104 mS/cm).

Nanocatalysts and Clusters

- DFT calculations of Pt_4 and Pt_3Co clusters shows that chemisorption of H_2 , O_2 , and CO molecules is energetically more favorable on the Co-doped cluster for all three diatomic molecules studied.
- For Pt_3Co clusters: H_2 undergoes dissociative chemisorption on the tetrahedral clusters in both head on and side on approaches to Pt centers; O_2 dissociation occurs in three and four center coordinations; and CO prefers to adsorb on Pt or Co atop atoms.
- Fuel cell catalyst annealing capability has been installed to permit replication of annealing procedures done at UTC Power, and both UNLV and UTC catalysts using soft X-ray and UV spectroscopies at UNLV and at the Advanced Light Source.

Future Directions

Theoretical Studies and Electronic Structure of Storage Materials

- Code development and testing will proceed to permit direct comparison of theoretical spectra with observations.
- Studies will continue of the properties of hydrogen multicenter bonds and how they may be harnessed to design novel hydrogen storage materials.
- Studies of hydrogen adsorption on metal-decorated nanomaterials will continue to study the local electronic structure of Li- and Ti-decorated SWCNTs by using STM and STS and to reproduce the area-integrating spectroscopic results.
- The influence of Ti and Li on the hydrogenation process will be studied.

Synthesis and Characterization of Mesoporous Conductive Polymer/Pd Concepts

- Research will continue to center on the evaluation and verification of hydrogen sorption of the composite materials produced using chemical and electrochemical methods.
- The role of $NaBH_4$ and its effects on the stability of treated materials will be addressed with effort to determine the chemical composition of the treated materials.
- Higher pressure measurements will be sought at Southwest Research Institute to obtain pressure and kinetic isotherms and determine if the materials meet DOE specifications.

Synthesis and Characterization of New Sulfonated Copolyamide Membranes for Fuel Cell Applications

- Synthesis of a new type of partially fluorinated sulfonated copolyamide with associated membrane properties will be undertaken to decrease the water uptake and improve water stability.

Nanocatalysts and Clusters

- Pt-Ru alloy systems will be investigated along with effects of catalyst-support interactions on catalytic activity; in this regard, calculations of the electronic structure of Pt-Co and Pt-Ru alloy clusters deposited on amorphous carbon is in progress.
- Pt_3Co and PtIr nanocatalysts from UTC will be prepared and measured at the Advanced Light Source and UNLV. Their electronic structure, especially the valence and conduction band and d-band center, will be compared to reference samples such as Pt, Co, and Ir metal.

FY 2008 Publications

- Xuezhi Ke and Changfeng Chen, "Thermodynamic functions and pressure-temperature phase diagram of lithium alanates by ab initio calculations", *Physical Review B* **76**, 024112 (2007).
- Yi Zhang, Hong Sun, and Changfeng Chen, New Template for Metal Decoration and Hydrogen Adsorption on Graphene-like C_3N_4 , submitted to *Physical Review Letters*; status: in revision.
- P.E. Kalita, S.V. Sinogeikin, K.E. Lipinska-Kalita, T. Hartmann, X.Z. Ke, C.F. Chen, and A.L. Cornelius, Equation of State of TiH_2 up to 90 GPa: a High-Resolution Synchrotron X-Ray Diffraction Study, submitted to *Physical Review B*; status: under review.
- Ravhi S. Kumar, Xuezhi Ke, Andrew L. Cornelius and Changfeng Chen, Effect of Pressure and Temperature on Structural Stability of Potential Hydrogen Storage Compound Li_3AlH_6 , Submitted to *Journal of Physical Chemistry B*; status: in press.
- P.F. Weck, E. Kim, S.S. Lepp, N. Balakrishnan, and H.R. Sadeghpour, Dimer-induced stabilization of H adsorbate cluster on BN(0001) surface, Physical Chemistry and Chemical Physics (Rapid communication, accepted).
- P. Tarakeshwar, T.J. Dhilip Kumar, and N. Balakrishnan, Hydrogen multicenter bonds and reversible hydrogen storage, *J. Am. Chem. Soc.* (under revision).
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- P. F. Weck, T. J. Dhilip Kumar, E. Kim, and N. Balakrishnan, "Computational study of hydrogen storage in organometallic compounds", *J. Chem. Phys.*, **126**, 094703 (2007).
- E. Kim, P. Weck, B. Naduvalath, and C. Bae, "Nanoscale Building Blocks for the Development of Novel Proton-exchange Membrane Fuel Cells", *J. Phys. Chem. B* **112** (Letter), 3238 (2008).
- G. Miller, J. Kintigh, E. Kim, P.F. Weck, S. Berber, and D. Tomanek, "Hydrogenation of Single-Wall Carbon Nanotubes using Polyamine Reagents: Combined Experimental and Theoretical Study", *J. Am. Chem. Soc.* **130**, 2296 (2008).
- E. Kim, R. Kumar, P.F. Weck, A.L. Cornelius, M. Nicol, S.C. Vogel, J. Zhang, M. Hartl, A. Stowe, L. Daemen, and Y. Zhao, "Pressure-induced phase transitions of $NaBH_4$: Theory and experiments", *J. Phys. Chem. B* **111** (Letter), 13873 (2007).
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- R. Kumar, E. Kim, and A.L. Cornelius, "Structural Phase Transitions in the Potential Hydrogen Storage Compound KBH_4 under Compression", *J. Phys. Chem. C*, **112**(22), 8452 (2008).
- P.F. Weck, E. Kim, S.S. Lepp, N. Balakrishnan, "Dimer-Induced Stabilization of H Adsorbate Cluster on BN(0001) Surface", submitted to PCCP (2008).
- E. Kim, P.F. Weck, S. Berber, and D. Tomanek, "Mechanism of graphitic nanocarbon hydrogenation by polyamines", submitted to PRB (2008).

FY 2008 Presentations

- "New Template for Metal Decoration and Hydrogen Adsorption on Graphene-like C_3N_4 ", Yi Zhang, Hong Sun, and Changfeng Chen, presented at the American Physical Society Annual March Meeting, March 12, 2008, New Orleans, LA.
- C. Heske and N. Balakrishnan, "Hydrogen Fuel Cells and Storage Technology Project", Presentation to the DOE Hydrogen Storage Tech Team, FreedomCAR, Detroit, April 17, 2008.
- C. Heske and N. Balakrishnan, "Hydrogen Fuel Cells and Storage Technology Project", Poster presentation at the DOE Program Review Meeting, Arlington, June 9, 2008.
- Balakrishnan Naduvalath, Hydrogen storage and catalysis, Presentation to Jesse Adams, DOE program Manager, during his site visit to UNLV on 03/14/08.
- P. Tarakeshwar, T.J. Dhilip Kumar, and N. Balakrishnan, Hydrogen Multicenter Bonds on Small Metal Clusters, APS March Meeting, March 10-14, 2008, New Orleans, Louisiana.

6. T.J. Dhillip Kumar, P. Tarakeshwar, and N. Balakrishnan, Sequential Dissociative Chemisorption of H₂ on Ti₁₃ Cluster, APS March Meeting, March 10-14, 2008, New Orleans, Louisiana.
7. P.F. Weck, E. Kim, C. Bae, and N. Balakrishnan Nanoscale building blocks for the development of novel proton-exchange membranes fuel cells: A first-principles study, APS March Meeting, March 10-14, 2008, New Orleans, Louisiana.
8. Euja Kim, Philippe Weck, Balakrishnan Naduvalath, Hansong Cheng, Boris Yakobson, First-Principles Study of Carbon Nanoframeworks Tailored for Hydrogen Storage, Hydrogen Multicenter Bonds on Small Metal Clusters, APS March Meeting, March 10-14, 2008, New Orleans, Louisiana.
9. P.F. Weck, E. Kim, N. Balakrishnan, H. Cheng, and B. Yakobson, *Lithium-coated carbon nanoframeworks tailored for hydrogen storage*, International symposium on material issues in a hydrogen economy, November 12-15, 2007, Richmond, Virginia.
10. Balakrishnan Naduvalath, *Fundamental studies of hydrogen storage and catalysis*, UNLV Energy Symposium, August 16, 2007, UNLV.
11. C. Heske, "Understanding and Optimizing Surfaces and Interfaces in Energy Conversion Devices", 2007 Annual Energy Symposium, UNLV, August 16, 2007 (invited talk).
12. Ich Tran, one of the two graduate students in our project, presented a poster at the 2007 Fall MRS Meeting in Boston, entitled: "Ti-coated Single-walled Carbon Nanotubes for Hydrogen Storage: A Spectroscopic and Microscopic Study".
13. C. Heske, "Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft x-ray spectroscopy", Chemical Engineering Department, University of California Santa Barbara, October 25, 2007.
14. C. Heske, "Surface and Interface Science on Devices for Energy Conversion", X-ray and Neutron Scattering Contractor's Meeting, Division of Materials Sciences and Engineering (DMS&E), DOE Office of Basic Energy Sciences (BES), Warrenton, VA, October 18, 2007.
15. C. Heske, "Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft x-ray spectroscopy", Cornell University, Materials Science and Engineering Department Seminar, October 11, 2007.
16. C. Heske, "Investigating the electronic and chemical properties of surfaces, interfaces, and other buried things with soft x-ray spectroscopy", Geoscience Department Seminar, UNLV, January 23, 2008.
17. C. Heske, "Soft x-rays and the electronic structure of buried things – interfaces, liquids, and below dirty surfaces", Materials Science Institute, University of Oregon, Eugene, February 26, 2008.
18. C. Heske, "Hydrogen Fuel Cells and Storage Technology Project", Presentation during the site visit of Jesse Adams, DOE Golden Field Office, on March 14, 2008.
19. C. Heske and N. Balakrishnan, "Hydrogen Fuel Cells and Storage Technology Project", Presentation to the DOE Hydrogen Storage Tech Team, FreedomCAR, Detroit, April 17, 2008.
20. C. Heske and N. Balakrishnan, "Hydrogen Fuel Cells and Storage Technology Project", Poster presentation at the DOE Program Review Meeting, Arlington, June 9, 2008.
21. E. Kim and T. Pang, "First-principles study of the oxygen-reduction reaction on the Pt (100) surface", 2008 APS March Meeting, New Orleans, Louisiana, March 10-14, 2008.
22. P. Weck, E. Kim, B. Naduvalath, and C. Bae, "Nanoscale building blocks for the development of novel proton-exchange membranes fuel cells: A first-principles study", 2008 APS March Meeting, New Orleans, Louisiana, March 10-14, 2008.
23. E. Kim, P.F. Weck, N. Balakrishnan, H. Cheng, B. Yakobson, "First-Principles Study of Carbon Nanoframeworks Tailored for Hydrogen Storage", 2008 APS March Meeting, New Orleans, Louisiana, March 10-14, 2008.
24. Savas Berber, David Tom'aneek, E. Kim, Philippe F. Weck, Glen P. Miller, "Hydrogenation of graphitic nanocarbons", 2008 APS March Meeting, New Orleans, Louisiana, March 10-14, 2008.
25. E. Kim, R. Kumar, A. Cornelius, M. Nicol, S. Vogel, J. Zhang, M. Hartl, A. Stowe, L. Daemen, and Y. Zhao, "Structural characterization of sodium borohydrides: Theory and Experiments", International Symposium on Materials Issues in a Hydrogen Economy, November 12-15 (2007), Richmond, VA.
26. R. Kumar, E. Kim, and A. Cornelius, "Structural changes in RbBH₄ under pressure investigated by Synchrotron powder X-ray diffraction and theoretical studies", International Symposium on Materials Issues in a Hydrogen Economy, November 12-15 (2007), Richmond, VA.
27. P. Weck, E. Kim, N. Balakrishnan, H. Cheng, and B. Yakobson, "Lithium-decorated carbon nanoframeworks tailored for hydrogen storage", International Symposium on Materials Issues in a Hydrogen Economy, November 12-15 (2007), Richmond, VA.