IV.H.5 Hydrogen Fuel Cells and Storage Technology Project*

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UTC Power, Inc, South Windsor, CT

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*Congressionally directed project

Objectives

- Study the electronic structure of nanomaterials for hydrogen storage to develop detailed understanding of hydrogen adsorption/absorption and desorption mechanisms.
- Investigate electronic structure, bonding and catalytic activities of pure and alloyed transition metal clusters for fuel cell applications.
- Collaborate with UTC in the development of efficient catalysts for fuel cell applications
- Develop new cost-effective hydrocarbon-based polymer electrolyte membranes with improved performance relative to Nafion®, especially at high temperature (120°C) and low humidity.

Technical Barriers

This project addresses the following technical barriers from the Storage and Fuel Cells sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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 Cells barriers addressed by this project:

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

Technical Targets

This project applies closely-coupled theoretical and experimental studies to gain fundamental understanding of hydrogen interaction with different nanostructured materials, fuel cell catalysis, and development of new fuel cell membrane materials. Topics of ongoing studies include:

- Hydrogen adsorption/desorption in various pure and doped matrices.
- The electronic structure of carbon nanostructures with metal adatoms including effects of adsorbed hydrogen molecules and atoms.
- Catalytic surface degradation mechanisms for fuel cell catalysts.
- Synthesis and performance of mesoporous polymer/metal nanostructures for hydrogen storage.
- Development of new sulfonated fuel cell membranes that meet DOE 2010 technical targets and that can outperform state-of-the-art Nafion® membranes at high temperature (120°C) and low relative humidity.
- Electronic structure, bonding, and dynamics and kinetics of adsorption/desorption processes.
- Hydrogen interaction, dissociation, and saturation on pure and alloyed transition metal clusters.

Accomplishments

- A detailed study of the adsorption of Ti and Li on carbon nanomaterials revealed oxidation

challenges of Ti adatoms that can be overcome by Li coadsorption.

- Studies of fuel cell catalysts prepared at UTC established their oxidation behavior as a function of annealing temperature and acid leach conditions.
- Synthesis and characterization of polyaniline/Pd composites established their potential for hydrogen storage.
- Fluorine substituted sulfonated proton exchange membranes (PEMs) performed better than Nafion® in proton conductivity and demonstrated acceptable water uptake.
- Quantified electronic structure, bonding, and hydrogen interaction and saturation of pure and alloyed clusters of Ti, Sc, and Zr.
- Investigated the role of external electric fields on hydrogen adsorption on transition metal clusters.

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Introduction

Design and development of improved low-cost catalytic materials and high-capacity hydrogen storage media are paramount to enabling the hydrogen economy. Presently available catalysts are mostly precious metals in pure or alloyed form and their high cost limits wider use in fuel cell applications. Similarly, materials with optimum hydrogen storage properties are yet to be designed. Both these properties are intimately linked to the electronic structure, morphology, size, etc. of the chosen materials. Here, we present results of combined theoretical and experimental studies of electronic structure, bonding, and hydrogen adsorption/desorption characteristics of a number of different nanomaterials and metal clusters. We further explore issues associated with oxidation of Ti-doped carbon-based materials and how oxidation can be minimized by doping with lithium. We also discuss the hydrogen storage properties of polyaniline/Pd composites synthesized at UNLV.

Most ionomer materials currently being tested in PEM fuel cells demonstration units are based on perfluorosulfonic acid (PFSA) polymers such as Nafion®. However, shortcomings of these materials seriously limit wide application of fuel cells as power sources. We discuss properties of new hydrocarbon-based high-performance sulfonated PEMs that can be manufactured at low cost.

Approach

We have performed deposition of metals (Ti and Li) on carbon nanomaterials (single-wall carbon nanotubes [SWCNTs] and C_{60}) under ultra-high vacuum (UHV) conditions and investigated the chemical and electronic structures using laterally integrating spectroscopic

techniques. The objectives are to understand the impact of the metal deposits on the surface of carbon nanostructures, the oxidation behavior of the metals, and the consequences for their application in hydrogen storage.

We have continued our studies of Pt-based fuel cell catalysts prepared at UTC and UNLV. The samples were measured using synchrotron- and lab-based soft X-ray and ultraviolet 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.

Pd/polyaniline composites were prepared using two different methods of Pd incorporation, namely chemical synthesis using either Pd(iv) or Pd(ii) and the monomer/oligomer, as well as electrochemical synthesis of polyaniline followed by reduction of Pd(iv) or Pd(ii).

Aromatic polyamides are known to have excellent chemical stability and mechanical properties that are critical features for an effective PEM in fuel cell applications. Initial results of sulfonated aromatic poly(ether amide) showed proton conductivity that is comparable to that of Nafion® at 80°C and 100% relative humidity. To improve proton conductivity of the membrane further while preventing excessive water uptake, synthesis efforts to incorporate fluorinated moiety along the polymer chains have been undertaken.

Results

X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy, and work function spectra of SWCNTs before and after Ti deposition show evidence of Ti-C bond formation. A similar interaction between Ti adatoms and C_{60} was observed and attributed to the hybridization of Ti 3d orbitals with the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of the C_{60} molecules. The deposited metallic Ti adatoms also strongly adsorb oxygen-containing species and become oxidized, even under UHV conditions. Figure 1a shows the increase of the O 1s XPS signal after the Ti-deposited SWCNT sample was stored in UHV ($\sim 10^{-10}$ mbar) for 2, 18, and 40 hours. Consequently, the metallic Ti adatoms were oxidized, as shown in Figure 1b, with the formation of Ti oxides. The oxidation of Ti is a great concern, because it would affect the suitability of the Ti-deposited systems as hydrogen storage materials. Primary results of a co-evaporation of Li and Ti on Au substrates have demonstrated that Li can be used to reduce Ti oxides after exposing the Ti-deposited sample to air. Thus, a co-evaporation experiment of Li and Ti was performed on a SWCNT sample to test whether a similar effect can be observed for SWCNT substrates. Indeed, preliminary XPS experiments confirm the reduction of the TiO_2 component and the re-appearance of the intermediate

(a) XPS Mg K$_\alpha$
O 1s
- SWNT
- Ti/SWNT-2h
- Ti/SWNT-18h
- Ti/SWNT-40h

Binding Energy (eV)

(b) XPS Mg K$_\alpha$
Ti 2p
- Ti/SWNT-2h
- Ti/SWNT-18h
- Ti/SWNT-40h

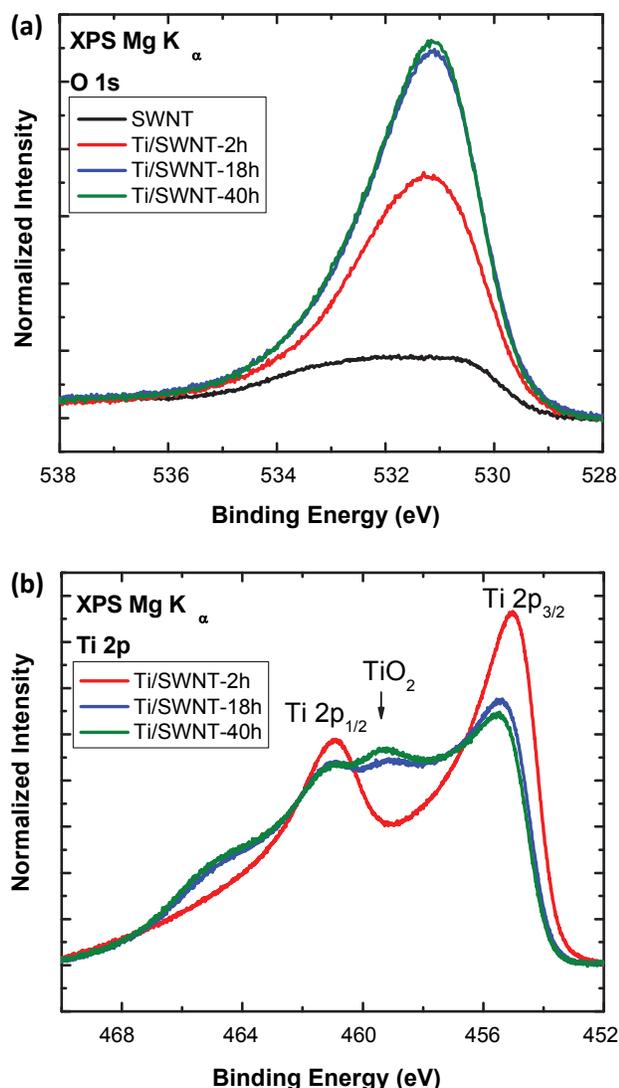Ti 2p$_{3/2}$
TiO$_2$
Ti 2p$_{1/2}$

Binding Energy (eV)

FIGURE 1. a) Increase of O1s XPS signal as a function of storage time in UHV (10^{-10} mbar) due to adsorption of oxygen species on the Ti-deposited SWCNTs; b) Oxidation of deposited Ti adatoms and formation of Ti oxides

XPS measured by monochromatic Al K$_\alpha$

O 1s   Pt 4p$_{3/2}$

Normalized Intensity (a. u.)

i. shipped from UTC annealed at 775 C mounted by carbon tape

ii. shipped from UTC annealed at 925 C mounted by carbon tape

iii. annealed under vacuum at 800 C mounted directly on Mo plate

iv. prepared at UNLV annealed at 925 C mounted by carbon tape

Binding Energy (eV)

FIGURE 2. O 1s and Pt 4p$_{3/2}$ XPS spectra of Pt$_3$Co/KB samples prepared at UTC and UNLV under different annealing temperatures and environments as listed (unless otherwise noted, samples were annealed under Ar flow). Spectra were normalized by the count rate at the low-binding energy side of the Pt 4p$_{3/2}$ peak.

Ti oxides and metallic Ti components after subsequent deposition of Li on the oxidized Ti/SWNT sample.

A new set of Pt-based bimetallic nanoparticle catalysts with carbon black support (PtIr/KB) prepared at UTC Power was studied using lab-based soft X-ray spectroscopies. The two measured samples were annealed at 700 and 1,000°C, respectively. Based on O 1s XPS spectra, the oxygen atoms in the samples exist in at least two different chemical environments, metal oxides and hydroxides. The overall O 1s peak area decreases with increasing annealing temperature, indicating that higher annealing temperatures are more effective in reducing the oxygen concentration on the nanoparticle catalysts. However, the presence of the metal oxides even after annealing suggest that
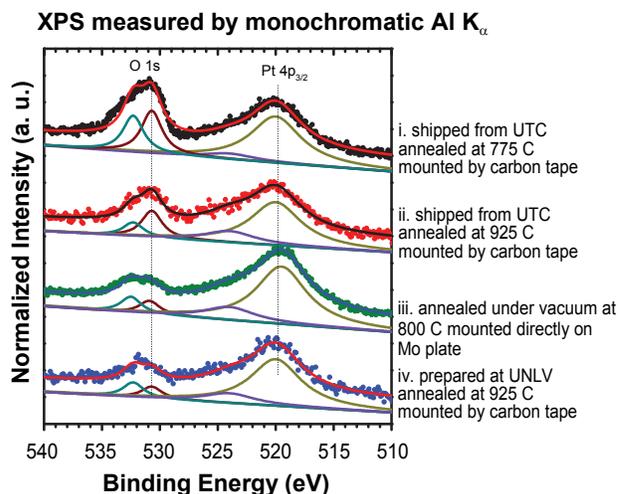
the current annealing process is not sufficient to fully remove the oxygen content from the samples. To address the impact of sample preparation process on the electronic structures of Pt-based bimetallic nanoparticle catalysts, we annealed Pt$_3$Co/KB samples at UNLV under either UHV environment or Ar gas flow, and compared to the samples shipped from UTC, which were annealed under Ar gas flow. Figure 2 shows O 1s and Pt 4p$_{3/2}$ XPS spectra of the Pt$_3$Co/KB samples, together with their optimized fits. Under similar sample preparation conditions, the sample annealed at lower temperature generally shows higher O 1s intensity than that annealed at higher temperature. The O 1s intensity of samples prepared at UTC is higher than that of samples prepared at UNLV, especially for the metal oxides component. This is likely due to additional oxidation during transit from UTC to UNLV. The origin of increasing oxygen content can be addressed by carefully examining the Pt 4p$_{3/2}$ feature, which also has two components: metallic Pt around 520 eV and Pt oxides around 524 eV. The ratio between these two components does not change more than 20% for the different samples, i.e., significantly less than the variation in oxygen intensity. Therefore, the increase of the O 1s intensity between samples prepared at the UTC and UNLV is interpreted as a result of oxidation of non-Pt metal components (likely Co in this case) and/or adsorption of oxygen-containing species on the carbon black during shipping. Furthermore, the O 1s spectrum from the sample annealed under vacuum has been obtained in situ at a base pressure of 5×10^{-10} mbar within two hours after the annealing process. Surprisingly, it shows a similar O 1s XPS intensity as the sample annealed under Ar flow (at higher annealing

temperature). This indicates that a reduction of the oxygen content in the annealing environment (i.e., vacuum vs. Ar flow) is helpful in reducing the oxygen content in/on the samples. However, even annealing in UHV is not sufficient to fully remove the oxygen from the samples.

On the theoretical side we investigated electronic structure, bonding, and hydrogen adsorption and desorption characteristics of several early transition metal clusters and their alloys with aluminum. Due to their high stability most of the calculations have been carried out on icosahedral clusters of Ti_{13}, Al_{13}, Sc_{13}, and Zr_{13} though larger 55 atom clusters have also been considered for Ti. It has been found that hydrogen saturation of these clusters with both icosahedral and octahedral geometries leads to multicenter hydrogen bonds (Figure 3(a) and (b)). These bonds are characterized by vibrational frequencies in the 1,100-1,500 cm^{-1} regime, which is quite distinct from vibrational frequencies associated with terminal hydrogen atoms on these metal clusters. One of the remarkable and novel features of hydrogen multicenter bonds is that the adsorbed hydrogen can be desorbed by vibrational excitation. While this has been experimentally demonstrated for desorption of molecular hydrogen from hydrogenated vanadium clusters and silicon surfaces, vibrational excitation could heat the metal clusters. However, mode-specific excitation could alleviate this problem and hence vibrational excitation of the infrared intense bands associated with hydrogen multicenter bonds may lead to desorption of the adsorbed hydrogen, enabling efficient reversible hydrogen storage. To gain mechanistic insights into the hydrogen adsorption process we are in the process of examining the transition states involved in the chemisorption reaction.

The calculations show that trace amounts of titanium dramatically alters the hydrogen binding capabilities of pure aluminum clusters, which might explain the role of titanium in the hydrogenation and dehydrogenation kinetics of complex metal hydrides. Figure 3(c) show the variation of the chemisorption energy with the composition of aluminum in $Ti_{13-n}Al_nH_{30}$ (n=1-6,12,13) clusters. Spurred by our recent findings that trace amounts of titanium in aluminum clusters dramatically enhance their ability to dissociatively chemisorb hydrogen, we explored the properties of several doped aluminum clusters. The choice of the dopant was dictated by experimental reports of the formation of alloys of these elements with aluminum. Our results indicate that hydrogen binding capabilities are dramatically enhanced by doping with iron or zirconium. This enhancement largely arises from the involvement of the d orbitals of the transition metal. Work is currently in progress to extend the findings of this study to other adsorbates like CO, O_2, and H_2O that are present in fuel cell environments.
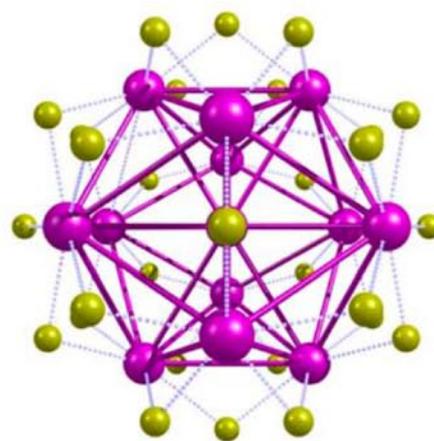
(a) $Ti_{13}H_{30}$
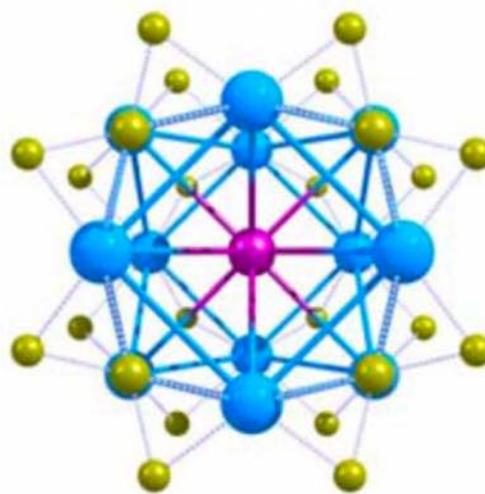
(b) $Al_{12}TiH_{24}$
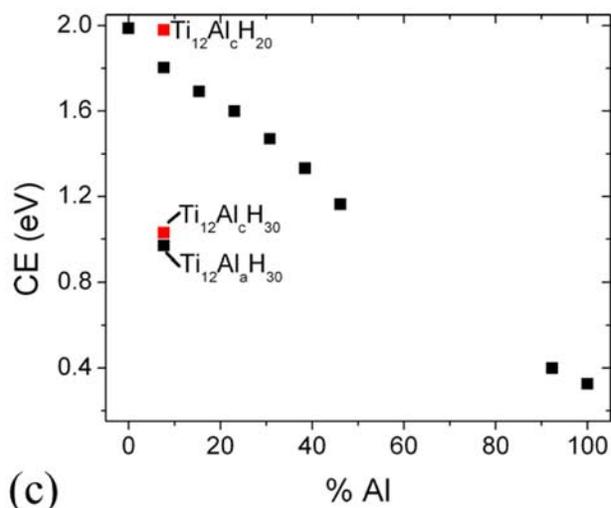
(c)

FIGURE 3. Optimized structures of (a) $Ti_{13}H_{30}$, (b) $Al_{12}TiH_{24}$ and (c) calculated chemisorption energies (ΔE_{CE}) of alloyed $Ti_{13-n}Al_nH_{30}$ (n=1-6,12,13) clusters.

We are also in the process of exploring the effect of an external electric field on hydrogen adsorption and saturation properties of transition metal clusters. Though there are extensive studies of interaction of small molecules with intense laser fields, there are no detailed experimental or theoretical studies of how hydrogen adsorption and desorption kinetics are modified in the presence of an external electric field. Our preliminary studies show that the effect of the electric field is to decrease the activation energy for hydrogen adsorption. This would also mean that the adsorbed hydrogen atoms can be desorbed at a lower temperature. This may have important consequences on hydrogen storage as well as catalytic properties of transition metal clusters as well as transition metal decorated nanostructures for hydrogen storage.

As part of the fuel cell membrane work, we prepared thin films of fluorine substituted sulfonated poly(ether amide)s (ODA-PFSA-xx and ODA-TFIPA-xx, where xx is the degree of sulfonation) and investigated their membrane properties. The fluorine substitution in the sulfonated polymers resulted in a significant reduction of water uptake level compared to that of non-fluorinated sulfonated polymers reported earlier. Even polymers with 90% sulfonation level (i.e., ODA-PFSA-90 and ODA-TIFF-90) exhibited acceptable levels of water uptake (30–40 wt%). Accordingly, we were able to incorporate higher concentration of sulfonic acid moiety into the polymer and synthesize PEMs with higher ionic exchange capacity (ion exchange capacity = 1.7–2.1 mequiv/g). The fluorine substituted ODA-PFSA and ODA-TFIPA series ionomers showed higher conductivity than the non-fluorinated polymer, ODA-SCPA-70, and Nafion® when measured at 100% relative humidity and different temperature (see Figure 4). The highest conductivity was obtained from ODA-TFIPA-90 (207 mS/cm at 80°C).

To date we have successfully prepared aniline/Pd materials using two different synthetic methods. Two of the materials produced showed very high hydrogen sorption at room temperature. This fact is important. Unlike some of the sorption based hydrogen storage materials reported in the literature, these materials do not require liquid nitrogen temperatures to observe hydrogen sorption. We have spent the last quarter evaluating the reproducibility of the sorption/desorption of hydrogen for the two most promising polyaniline /Pd composites. Hydrogen sorption data is presented in Figure 5.
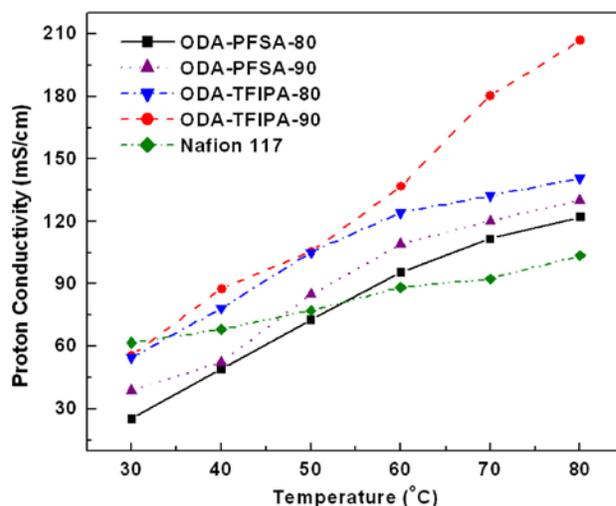

FIGURE 4. Proton conductivities of fluorine substituted sulfonated poly(ether amide)s and Nafion®.
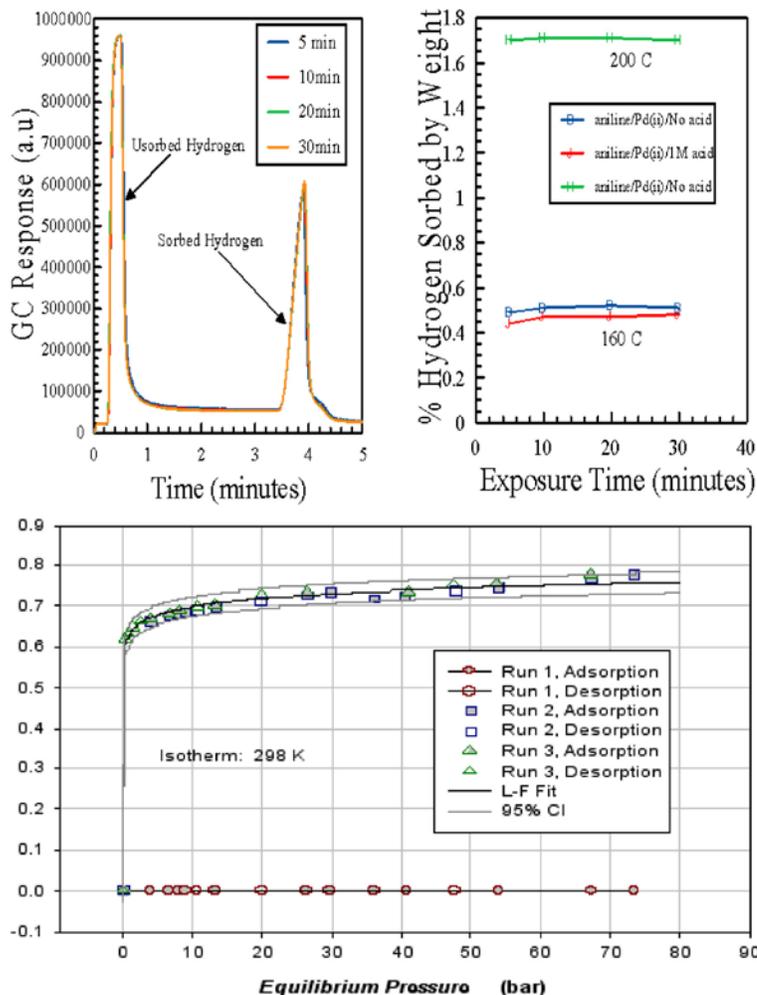

FIGURE 5. Left: Hydrogen sorption at Aniline/Pd(ii) composite. Right: Percent hydrogen sorption at Aniline/Pd(ii) composite as a function of exposure time at desorption temperatures of 200ºC and 160ºC. Bottom: Hydrogen sorption/desorption isotherms for Aniline/Pd(ii) composite measure independently by Southwest Research Institute®.

The unsorbed hydrogen elutes in less than one minute with the sorbed hydrogen observed at ~3.5 minutes. In addition the exposure times do not result in large differences in sorbed hydrogen indicating fast kinetics. The adsorption/desorption isotherm for the composite is presented in Figure 5, bottom. This data shows maximum hydrogen sorption of 0.8% for the composite held at room temperature, as a function of equilibrium pressure. The results verify the sorption values obtained in our laboratory for the composite material. More importantly, the percentage of hydrogen sorption observed for the composite is the highest obtained at room temperature for any material in the literature to date.

Conclusions and Future Directions

Our studies of hydrogen adsorption on metal-decorated nanomaterials will be continued. One goal is to study the local morphology and electronic structure of Ti-decorated SWCNTs by using scanning tunneling microscopy and scanning tunneling spectroscopy. Furthermore, the influence of Ti and Li on the hydrogenation process will be studied by spectroscopy techniques at UNLV as well as with our new high-resolution photoemission setup at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. We hope to carry out theoretical studies to gain more insights into this as well as the role of alloying and external fields on hydrogen adsorpion/desorption kinetics.

Pt$_2$IrCo supported by graphitized Vulcan XC-72 will be measured at ALS and UNLV. Their electronic structure, especially the valence and conduction band and the d-band structure will be compared to reference samples such as Pt, Co, and Ir metal.

Durability test of the new developed PEMs and incorporation of fluorine substituents into sulfonic acid moiety instead of polymer main chain are suggested.

FY 2009 Publications/Presentations

Presentations

1. I. Tran, R. Felix, Y. Zhang, M. Bär, C. Heske, and L. Weinhardt, "Microscopic and Spectroscopic Studies of Metal Deposition on Carbon Nanomaterials", with New Diamond and Nano Carbons Conference (NDNC 2009), June 7–11, Traverse City, MI (poster).

2. C. Heske, "How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces", ALS/CXRO Seminar Series, Lawrence Berkeley National Laboratory, Berkeley, May 13, 2009.

3. C. Heske, "How soft x-ray spectroscopy can shed light on the electronic and chemical properties of interfaces," PIRE-ECCI (Partnership for International Research and Education) Seminar, Electron Chemistry and Catalysis at Interfaces, Department of Chemistry and Biochemistry, University of California, Santa Barbara, November 5, 2008.

4. C. Heske, "FCAST - The Fuel Cell and Storage Technology Project at UNLV", 2008 Annual Energy Symposium, UNLV, August 20, 2008.

5. C. Heske, "How soft x-ray spectroscopy can help the 'Hydrogen Economy' (hopefully)", Seminar Experimentelle Physik II, University of Würzburg, Germany, July 8, 2008.

6. R. Felix, I.C. Tran, L. Weinhardt, M. Bär, T. Hofmann, Y. Zhang, and C. Heske, "Study of the Interaction between Hydrogen and Carbon-based Nanomaterials",2008 MRS Fall Meeting, Boston, Dec. 1–5, 2008 (Poster). Selected for Best Poster Award ($500).

7. Y. Zhang, "The chemical and electronic structure of platinum-based nanoparticle catalysts for PEM fuel cells", 2008 American Chemical Society Western Regional Meeting, Las Vegas, Sept. 24–27, 2008 (Invited Oral).

8. T.S. Jo, C. Bae, "Synthesis of Ionic Conducting Polymers for Fuel Cell Applications and Biodiesel Productions" 42nd Western Regional Meeting of the American Chemical Society, Las Vegas, NV, September 23–27, 2008.

9. C. Bae, "New Functional Polymers for Alternative Energy Application" UNLV Renewable Energy Symposium, Las Vegas, NV, August 20, 2008.

10. Tarakeshwar Pilarisetty, Dhilip Kumar Thogluva Janardhanan, and N. Balakrishnan, Hydrogen storage and catalytic properties of transition metal clusters: Bonding changes and saturation effects, 236th American Chemical Society National Meeting, Philadelphia, PA, August 17–21, 2008.

11. T.J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, Geometric and Electronic Structures of Ti-Al and Hydrogenated Ti-Al Nanoclusters, American Chemical Society Western Regional Meeting, Las Vegas, NV, September 24–28, 2008.

12. T.J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, The Effect of Alloying on CO Tolerance of Pt Nanoparticles, American Chemical Society Western Regional Meeting, Las Vegas, NV, September 24–28, 2008.

13. Huy Mai, T.J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, Computational Studies of H$_2$, O$_2$, and CO Adsorption on Pt and Pt-Ru Catalyst Clusters for Hydrogen Fuel Cell Applications, American Chemical Society Western Regional Meeting, Las Vegas, NV, September 24–28, 2008.

Publications

1. I. Tran, Dissertation, Department of Chemistry, UNLV: "Microscopic and Spectroscopic Studies of Metal Deposition on Carbon-based Materials", November 2008.

2. T.S. Jo, C.H. Ozawa, B.R. Eagar, L.V. Brownell, D. Han, and C. Bae, "Synthesis of Sulfonated Aromatic Poly(ether amide)s and Their Application to Proton Exchange Membrane Fuel Cells", *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2009**, *47*, 485–496.

3. P.F. Weck, E. Kim, S. Lepp, N. Balakrishnan, and H.R. Sadeghpour, Dimer-induced stabilization of H adsorbate cluster on BN(0001) surface, Physical Chemistry and Chemical Physics, **10**, 5184 (2008).

4. P. Tarakeshwar, T.J. Dhilip Kumar, and N. Balakrishnan, Hydrogen Multicenter Bonds and Reversible Hydrogen Storage, *J. Chem. Phys.* **130**, 114301 (2009).

5. T.J.Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, Geometric and electronic structures of hydrogenated transition metal (Sc, Ti, Zr) clusters, Phys. Rev. B **79**, 022703 (2009).