IV.G.1 Hydrogen Fuel Cells and Storage Technology Project (FCAST)*

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*Congressionally directed project

Objectives

Create a framework for interdisciplinary academic research that combines theory and experiment to address specific fundamental aspects of hydrogen storage and utilization.

Quantify:

- Electronic structure, density of states and pseudo-potential functions for defined storage media.
- The mechanisms of hydrogen adsorption/desorption in potential storage materials.
- Catalysis of hydrogen adsorption and dissociation on platinum/platinum alloy surfaces.

Optimize:

- Specific capacity of carbon and boron-nitride storage matrices of different structures and compositions.
- Operating temperatures and durability of hydrogen fuel cell catalytic surfaces.

Demonstrate specific capacity storage performance and catalytic surface degradation mechanisms for selected configured materials.

Technical Barriers

This project addresses the following technical barriers from 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

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 nanomatrices.
- 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.

These capabilities will be combined and applied to rapid assessments of gravimetric capacity, usable specific energy and storage media durability and operability for varieties of storage material, both conceptual and realized. Success in this venture will provide the program with process understanding at the fundamental level and performance prediction with adequate confidence to support Hydrogen Storage Program planning decisions.

Accomplishments

- Developed new data acquisition software and implemented with new, high resolution spectrometer at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, in collaboration with the University of Wurzburg to acquire complete resonant inelastic X-ray scattering spectra (RIXS) maps with unprecedented resolution in remarkably reduced experimental time.
- RIXS of C_{60} acquired and first density functional theory (DFT) calculations of C_{60} obtained for comparison. Complete band structure calculations using the GW approximation are in progress for detailed validation.
- Nanowire matrices of catalytic materials successfully synthesized inside nanoporous alumina as precursor material for the fabrication of matrices of carbon nanotubes and other materials.
- Specialized equipment for the fabrication of high quality carbon nanotubes installed and preliminary deposition of carbon nanotubes was successfully carried out using thermal chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD).
- Stable structures of graphitic BC_2N identified and DFT using the GW approximation predicted band gap in excellent agreement with measured values.
- Systematic study of hydrogen storage capacities of transition metal-organic systems (M-C_4H_4, M-C_5H_5, and M-C_6H_6, M= Sc, Ti, V) performed. ScC_4H_4 predicted to provide 9.3 wt% H_2 storage with average binding energy of 0.33 eV/H_2.
- Molecular dynamics simulation of a novel three-dimensional single-wall carbon nanotube (SWCNT) nano-framework functionalized with phenyl spacers predicted to be stable up to 600 K.
- Observed oxidation of Ti-decorated nanomaterials even in ultra-high vacuum.
- Applied first principles electronic structure and lattice dynamics calculations to establish the reaction paths and phase diagrams of $LiAlH_4$ and Li_3AlH_6.
- Achieved the first one-pot chemical synthesis of Pd-doped polyaniline (PANI/Pd) using $PdCl_6^{2-}$ anion as the only chemical oxidant and scaled the process to produce bulk quantities with optimum electronic properties.
- Scanning electron microscopy (SEM) showed the expected porous structure and hydrogen sorption experiments with PANI/Pd are underway.
- Synthesis and characterization of four examples of high molecular weight sulfonated aromatic polyamides for fuel cell membrane utilization.
- Studied the effect of adsorption of H_2, O_2 and CO molecules on different catalyst binding sites such as Co end, Pt end, Co-Pt bond, Pt-Pt bond and Pt-Co-Pt face of optimized tetrahedral Pt_3Co clusters.
- Experimental characterization showing that Co tends to lie beneath the Pt surface in PtCo fuel cell catalyst nanoparticles confirmed by preliminary theoretical calculations.
- Substrate effects on electronic structures of deposited Pd and Pt nanoclusters have been analyzed theoretically.

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Introduction

The long-term goal of this project is to apply a science-based framework to determining the maximal achievable specific storage capacity of a variety of solid state materials and concepts. For this purpose, we combine a number of different experimental and theoretical approaches, such that, in close collaboration and mutual verification between theory and experiment, a solid fundamental base can be established to enable rapid assessment of different materials and structures.

Among the different methods of hydrogen storage, nanomaterial matrices offer a compromise considering both safety and cost if their original promise can be realized. Carbon-based matrices have attracted large attention because of theoretically predicted very high numbers of (reversibly) adsorbed hydrogen molecules per unit surface area or per adsorbate (metal) atom. 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 work on nanotubes has explored hydrogen adsorption mechanisms by physisorption and chemisorption. Some studies have shown a strong temperature dependence of physisorption in nanotubes and high adsorption at elevated temperatures, while the results of other studies favor low temperatures. A transition from sp^2 to sp^3 bond types during chemisorption has been reported in nanotubes and theoretical work shows application of external pressure enhances the bonding characteristics. This raises the question whether kinetic barriers might inhibit bonding in the experiments. Therefore, thermal energy can help to overcome this barrier while elevated pressure may support bonding.

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. More cost-effective fuel cell components are expected to result from better understanding of the physical and chemical nature of catalyst performance, the characterization of oxidation and reduction processes on system surfaces and the development of improved mechanical and thermal stability of high performance proton exchange membranes.

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. For this purpose, we combine a number of different experimental and theoretical approaches, such that, in close collaboration and mutual verification between theory and experiment, a solid fundamental base can be established for rapid concept evaluation.

The 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, as well as providing a comprehensive data base of H-H_2, H_2-H_2 collisional rate coefficients over a wide range of temperature with thermal and nonthermal populations of H_2. Accurate calculations of catalytic dissociation of H_2 on Pt and Pt-Co alloys will also be performed.

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). They collaborate closely with the theoretical tasks of this project. The ultimate goal is to verify theoretical predictions and to introduce new aspects into the fundamental calculations which will help the project in reaching the goal of determining suitable solid state materials for efficient hydrogen storage and permeation.

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

In the past year, material characterization efforts have emphasized the development and optimization of nanotube sample preparation, collecting atomically resolved images of nanotube material, and investigating nanotube materials with spectroscopic methods. In all of these studies, we have utilized our microscopic and spectroscopic techniques at UNLV and at the ALS.

Carbon-Based Hydrogen Absorption and Desorption Studies

Electro-deposition of nanotubes was developed for preparing suitable samples for the scanning probe microscope (SPM). Nanotubes dispersed in water are brought between a highly-ordered pyrolytic graphite (HOPG) substrate and a stainless steel plate. The nanotubes are then deposited by applying a voltage between HOPG and the steel plate. We find that, using optimized deposition parameters and geometry, this approach provides sparse coverage of SWCNT on the HOPG surface as shown in Figure 1. These samples exhibit individual nanotubes on a flat surface, which is ideal for the investigation of hydrogen adsorption on SWCNTs with SPM. With high magnification, we find occasionally that small bundles (e.g. two bundled

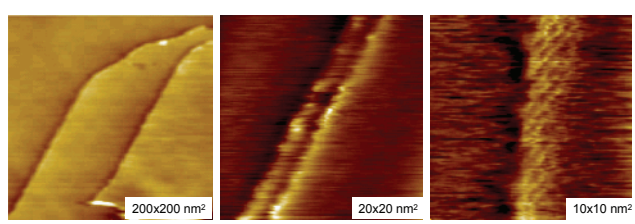

FIGURE 1. Scanning Tunneling Microscopy Images of SWCNT Electrodeposited on HOPG Surface (Left: two individual nanotubes; center: "bundle" of two SWCNTs; right: atomic resolution of a single SWCNT.)

tubes, see middle picture of Figure 1) are formed. We were able to observe individual (i.e., isolated) SWCNTs and achieve atomic resolution, as shown in the right image in Figure 1. We have successfully extended these experiments by using Au-coated Si wafer substrates to enhance the image contrast between nanotubes and substrate. By using such samples first tunneling spectra (i.e., local current-voltage curves, scanning tunneling spectroscopy) could be collected. This technique gives us the possibility to investigate the electronic structure of a single nanotube, alleviating the well-known problems of heterogeneity of starting materials. The local tunneling spectra can be correlated to the structural parameters of the chosen nanotube (in particular the chirality and the diameter).

One approach to enhance the hydrogen storage capabilities of carbon nanomaterials is functionalization with Ti atoms. Previously, only theoretical investigations of this concept existed. We have performed first experiments by depositing Ti onto SWCNT films in our ultra-high vacuum (UHV) instrument at UNLV (base pressure 4 x 10^{-10} Torr). The Ti/SWCNT samples were then investigated *in situ* using X-ray photoelectron spectroscopy (XPS). The survey spectrum of the Ti/SWCNT sample shows the Ti lines, as expected, but in addition, also a strong increase of the O 1s intensity, pointing towards an oxidation of Ti. This can be explained by the fact that the Ti surface is very reactive and is rapidly covered by adsorbates even under UHV conditions. In fact, Ti-covered surfaces are commonly used as pumps for UHV applications, where an evaporated Ti layer gets renewed every few hours (the so-called "Ti sublimation pump"). The finding of a very reactive Ti layer is supported by the Ti 2p detail XPS spectra presented in Figure 2 on the right-hand side. By comparing with literature values, the Ti compound found shortly after Ti deposition seems already be partly oxidized as TiO. When subsequently heating the sample, a second chemical Ti species emerges, namely TiO_2. This indicates an increasing oxidation of the Ti film. The

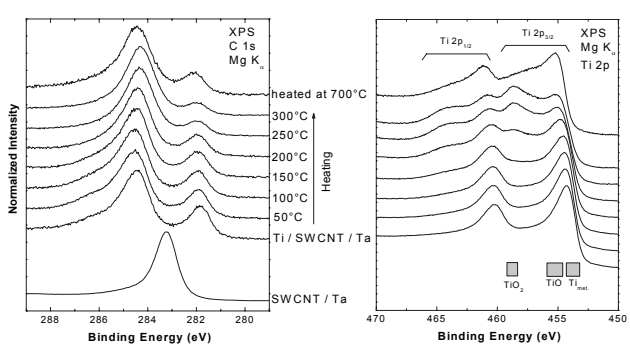

FIGURE 2. XPS C 1s (left) and Ti 2p (right) Detail Spectra of SWCNT/Ta and Ti/SWCNT/Ta after Heating for 1 hour at the Indicated Temperatures (Reported Ti $2p_{3/2}$ line positions are indicated by the rectangles on the right.)

comparison with a sample which was only heated once (but at a much higher temperature) suggests that the actual temperature during the heating is less important than the total exposure time of the surface (as expected).

The C 1s detail spectra presented in the left-hand part of Figure 2 reveal dramatic changes after the deposition of Ti. Several different (at least three) C species can be identified after Ti deposition, none of which coincide with the C 1s line position in the pure SWCNT/Ta sample. This indicates a strong interaction between Ti and C. The additional carbon components can presumably be attributed to adsorbates on the Ti surface.

An atomic hydrogen source was designed and constructed, and first experiments are ongoing. By electron-beam bombardment, we have been able to achieve 1850°C at a hydrogen-gas-emitting tungsten capillary, which is higher than the required temperature for hydrogen cracking. Currently, we are performing first adsorption experiments of atomic hydrogen on SWCNTs.

First-principles calculations were used to determine the structural stability of a number of light-element B-C-N materials as possible templates for high-capacity reversible hydrogen storage media. These materials include BC_2N, B-C, and C-N compounds in various structural forms, such as nanoclusters, nanotubes, graphitic phases and bulk phases (surfaces). They exhibit a rich variety of bonding configurations. In particular, the boron and nitrogen sites provide the local bonding environments that may lead to improved binding energy for transition metal adsorption or even direct hydrogen adsorption. Both direct hydrogen adsorption and hydrogen adsorption after transition metal decoration were explored. The results indicate that the boron and nitrogen atoms introduce significant changes in the local bonding environments that affect the binding energy of the adsorbed hydrogen molecules in very different ways, suggesting that nitrogen atoms have a negative influence on hydrogen storage in such materials because its excess electrons tend to destabilize the hydrogen adsorption. Boron atoms appear to play a positive role in hydrogen adsorption. This knowledge forms the basis of a thorough understanding of the interaction of hydrogen with the B-C-N system that is important for the design of practical hydrogen storage materials. The energetics of different adsorption sites were compared and evaluated for potential applications. Bonding variation and charge transfer were specifically studied to reveal their influence on the binding energy and relative stability of various configurations for transition metal decoration and the subsequent hydrogen adsorption. Systematic searches have been conducted to identify optimal material and doping configurations for stable and reversible hydrogen storage near ambient temperature and pressure conditions. We are currently in the process of analyzing a large set of recent data.

Concrete results and conclusions on the hydrogen adsorption in these materials will be drawn from the data and new materials may be identified for improved hydrogen storage performance. A manuscript is in preparation for submission to a peer reviewed journal.

Another computational effort has produced the density of states and the electronic band structure of C_{60} arrays over the entire Brillouin zone. The data provide a theoretical framework for analyzing the experimental results obtained by the experimental runs at the ALS. We have collected a large dataset of X-ray emission and absorption spectra of different carbon nanomaterials (i.e., SWCNT, MWCNT, C_{60}). Taking advantage of a new X-ray spectrometer, which was developed by the University of Würzburg in close collaboration with our group, complete X-ray emission "maps" could be collected. Such maps represent a clear quantum leap in X-ray emission spectroscopy (XES) and have previously not been possible due to transmission and resolution limitations of the soft X-ray spectrometers. The maps, whose analyses are currently in progress, will give unprecedented detailed insight into the electronic structure of the investigated materials.

Carbon Nanoframeworks

We are studying a novel class of 3-D materials consisting of ultrasmall diameter SWCNTs covalently functionalized by organic ligands as potential hydrogen storage media. Specifically, we have carried out DFT calculations to determine the stable structures and properties of nanoframeworks consisting of (5,0) and (3,3) SWCNTs constrained by phenyl spacers (cf. Figure 3). Valence and conduction properties, as well as normal modes, of pristine nanotubes are found to change significantly upon sp^3 rehybridization of the sidewall carbon atoms resulting from covalent functionalization. It has been reported recently that such nanoframeworks can be produced experimentally by growing selectively arrays of (5,0) and (3,3) SWCNTs in the channels of zeolite crystals (AFI) by pyrolysis of tripropylamine (TPA). *Ab initio* Car-Parrinello molecular dynamics (MD) simulations indicate that the proposed nanoframeworks are energetically as well as thermodynamically stable up to at least 600 K. Our results have been published in Weck et al., Chem. Phys. Lett. 439, 354 (2007) and presented at the 2007 APS March meeting.

The large accessible area characterizing this new class of materials should be favorable for hydrogen storage and the short hydrogen diffusion paths in such nano-sized structures are expected to promote hydrogen release with diffusion coefficients typically higher than in polycrystalline materials. In order to increase the hydrogen uptake in the interstitial cavity of such nanoframeworks, we are using DFT calculations and MD simulations to study the possibility of Li-atom deposition on the sidewalls of the carbon nanoframeworks (cf. Figure 4), which can be accomplished by practical experimental methods such as the covalent sidewall functionalization in a Li/NH_3 expansion solvent recently developed at Rice University by Tour and co-workers.

Carbon Nano-Structure Synthesis

This synthesis approach is attempting to implement nanowire matrices of carbon nanotubes (CNTs) and nanotubes of other suitable materials (e.g., BN) embedded in nanoporous alumina. The original approach attempted to incorporate already synthesized CNTs inside nanoporous alumina by electrophoresis. Charged CNTs were obtained and electrophoresis was applied inside the nanoporous matrix of a thin film alumina template. The samples were then extensively characterized using field emission scanning electron microscopy. However, only a few CNTs were observed partially inside the nanoporous matrix and surface coverage of the alumina matrix with CNTs was a dominant feature. A possible reason is the large aspect ratios of the CNTs that makes nanoporous alumina

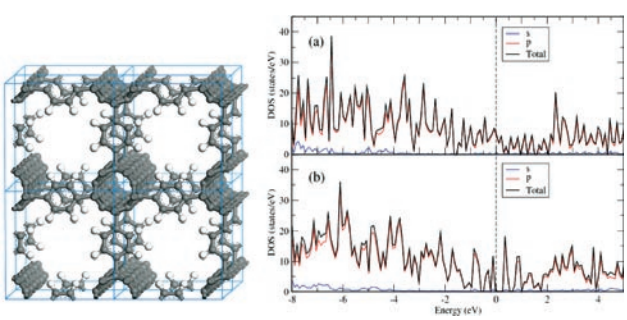

FIGURE 3. Left: Optimized Nanoframework Structure Consisting of (5,0) SWCNTs Constrained by Phenyl Spacers Right: Total and S- and P-Projected Densities of States of (a) a Pristine (5,0) SWCNT, and (b) the Corresponding Nanoframework

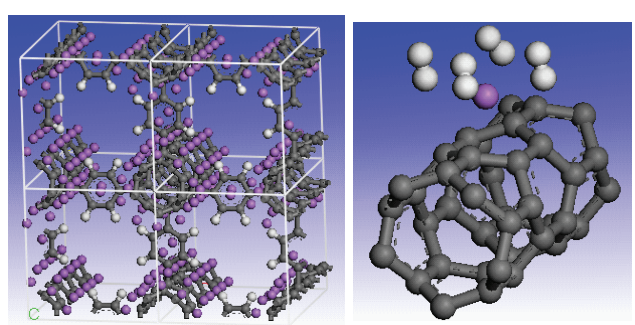

FIGURE 4. Left: Optimized Li-Coated Nanoframework Structure Consisting of (5,0) SWCNTs Constrained by Phenyl Spacers Right: Relaxed Geometry of a (5,0) Tubule Decorated by a Li Atom Binding up to 4 H_2 Molecules by Kubas-Type Interactions

inclusion difficult. While electrophoresis remains a promising method due to its simplicity, another approach of direct synthesis of nanotubes inside the nonporous matrix has been selected. Specialized equipment was designed, built and installed for this purpose. The equipment is an extension to the UNLV nanodeposition system that includes the ability for PECVD and thermal CVD without exposing the samples to atmosphere. Preliminary deposition of CNTs has been performed. The process parameters for CNT deposition are currently being optimized to improve the uniformity of CNT coverage. A new technique for the synthesis of high quality CNT matrices makes use of a radio frequency (RF) atom source. The RF atom source has been obtained and integrated with the UNLV nanodeposition system. Process parameters are currently being optimized for the growth of high quality CNTs.

Organometallic Systems

We performed a systematic computational study of the hydrogen storage capacity of model organometallic compounds consisting of Sc, Ti, and V transition metal atoms bound to C_mH_m rings (m=4–6). For all the complexes considered, the hydrogen storage capacity was found to be limited by the 18-electron rule. The maximum retrievable H_2 uptake predicted is 9.3 wt% for ScC_4H_4, slightly better than the 9.1 wt% hydrogen for TiC_4H_4, and much larger than the ~7 wt% hydrogen for VC_4H_4, where only four H_2 molecules can be adsorbed. The kinetic stability of these hydrogen-covered organometallic complexes has been reviewed in terms of the energy gap between the highest occupied and lowest unoccupied molecular orbitals and the strength and nature of successive H_2 bindings. Our findings were published in J. Chem. Phys. (2007).

Metal Hydride Studies

Solid metal hydrides are a promising class of materials for hydrogen storage. They have attracted a lot of interest in recent years. However, many questions remain concerning their thermodynamic behavior and the underlying atomistic mechanisms that are critical for further improvement of their performance. We have recently developed theoretical and computational capabilities to perform first-principles calculations of thermodynamic properties of solid metal hydrides. Most energetic calculations reported in the literature are performed at absolute zero temperature (i.e., 0 K). However, practical mobile applications of such materials will inevitably involve finite (even quite high) temperature and pressure. It is therefore critical that the thermodynamic behavior of hydrogen storage materials be examined and understood. We have completed an extensive computational study of the thermodynamic properties of lithium alanates. The obtained thermodynamic functions are in excellent agreement with available experimental data. The full set of calculated thermodynamic functions provides a reliable basis for the construction of the pressure-temperature phase diagram of these materials. It allows the examination of the hydrogen adsorption and desorption processes under realistic operating conditions in anticipated applications. We have implemented such calculations and examined the stability and reversibility of hydrogen storage in several lithium alanates and identified the phase boundaries for reversible hydrogen storage. The calculated thermodynamic functions also provide a reliable data set for empirical simulations and engineering modeling at much larger scales. This work will appear in *Physical Review B*. The developed computational methods can be applied to other hydrogen storage materials for the study of their thermodynamic properties and phase diagrams in an effort to identify new materials with improved performance under desired pressure and temperature conditions for applications.

Mesoporous Conductive Polymer Storage Research

The uptake and storage of hydrogen in conductive polymers is based on its high intrinsic electron density and the ability to dope the materials with protons, anions, and metal species. Previous studies with conductive polymer systems have been contradictory. In one case the uptake of 7 to 8% hydrogen is reported. Another study reported no ability to store hydrogen. Modification of the polymer with Pd metal has been proposed to enhance its storage capacity. There is conflicting literature regarding the incorporation of Pd into polyaniline. The methods used to incorporate the Pd species are:

1. Chemical synthesis using either Pd(iv) or Pd(ii) and the monomer/oligomer.
2. Electrochemical synthesis of PANI followed by reduction of Pd(iv) or Pd(ii).

Each method produces different materials with varying composition of Pd. The last year has been focused on determining the Pd species oxidation state in the materials produced using methods 1 and 2. The reaction of aniline with Pd(ii) does not necessarily produce the polymer/metal composite. Rather, a Pd/aniline complex results from the chemical synthesis. However, we used chemical methods to complex to the composite. Treated samples are shown in Figure 5. We have evaluated the percent of polymer versus Pd so that we can measure the hydrogen sorption with respect to the percent polymer and grams of Pd in the composite. Studies were conducted to ascertain the oxidation state of the metal and the reactivity of the metal after incorporation into the polymer. The goal is to enhance the properties of the Pd based on the high electron

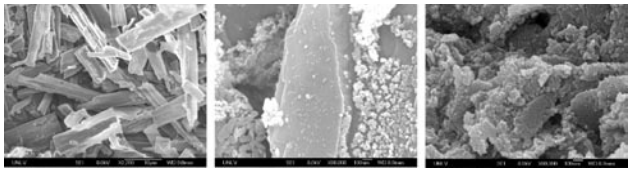

FIGURE 5. Pd(ii)/Aniline Complex (left) The planar sheets of material are between 100 – 250 nm wide. Pd(ii)/aniline after reduction with $NaBH_4$ (middle). The material shows both the granular polymer/metal composite and the planar sheets indicating only partial reduction of the dimer to Pd metal and polymer. Pd(iv)/aniline material (right). The material is granular in nature with the absence of planar sheets.

density of the conducting polymer. The activity of the Pd species will be probed through catalytic studies. Finally, we have designed an in-house hydrogen sorption apparatus to measure the uptake/expulsion of hydrogen for the synthesized materials. These experiments are currently underway.

Sulfonated Polyamide PEM Studies

During the second year of this subtask, postsulfonation of aromatic polyamides was initially attempted to prepare PEMs for fuel cell application. Unfortunately, similar to the result found in literatures of postsulfonation of polymers, the harsh sulfonation condition (e.g., fuming sulfuric acid, concentrated sulfuric acid as solvent and sulfonating reagent) caused only degradation of the polymers. As an alternative way to synthesize sulfonated polyamides, polycondensation reactions of sulfonated diamine with dicarboxylic acid chlorides or dicarboxylic acids were conducted. Although this route produced sulfonated polyamides successfully, the molecular weights of the polymers estimated by measuring intrinsic viscosity were not high enough (intrinsic viscosity ~0.5 dl/g) to be used as a tough membrane in proton exchange membrane fuel cells. Finally, as shown in Figure 6, polycondensation of diamines and sulfonated dicarboxylic acids under optimized condition produced high molecular weight sulfonated aromatic polyamides (**1a** – **1d**). Their intrinsic viscosities were 4.6–7.4 dl/g for para-substituted polymers (**1a**, **1c**, **1d**) and 1.5 dl/g for meta-substituted polymer (**1b**) in dimethyl sulfoxide (DMSO) solution containing 5% LiCl. The chemical structures of the polymer electrolytes were confirmed by nuclear magnetic resonance spectroscopies (^1H, ^{13}C) and Fourier transform infrared (FTIR) spectroscopy. Tough thin films (~0.1 mm thickness) of the polymer electrolytes were prepared by casting the polymer solution onto a clean glass plate. Proton conductivities of the membranes are currently being measured using a BekkTech (Loveland, CO) Proton Conductivity Measurement System at 60°C under different relative humidity condition (25% to 100%) and its result will be studied in relation with membrane properties.

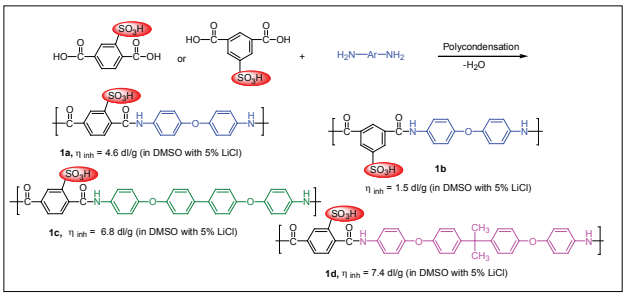

FIGURE 6. Polycondensation of diamines and sulfonated dicarboxylic acids under optimized condition produced high molecular weight sulfonated aromatic polyamides (**1a – 1d**). Their intrinsic viscosities were 4.6–7.4 dl/g for para-substituted polymers (**1a, 1c, 1d**) and 1.5 dl/g for meta-substituted polymer (**1b**) in DMSO solution containing 5% LiCl.

DFT structural calculations of the conformations of these new polymers have been performed. Specifically, we have shown the important effect of CF_2 groups inserted in the Teflon® backbone on the polymer conformations. In addition, we have investigated the effect of humidity and acidity on the conformations of the different polymers proposed. Using *ab initio* molecular dynamics simulations, we have studied the deprotonation process of the sulfonic acid groups connected to the polymer backbone.

Fuel Cell Catalytic Materials Research

In collaboration with UTC Power, first principles calculations of the electronic structure of small clusters of Pt-Co alloy are in progress. The effect of adsorption of H_2, O_2, and CO molecules on different binding sites such as Co end, Pt end, Co-Pt bond, Pt-Pt bond and Pt-Co-Pt face sites of the optimized tetrahedron Pt_3Co cluster have been studied. A manuscript describing these calculations is in preparation. In a related work, we are studying the composition and crystal structure of Pt_3Co/C alloy sample provided by UTC Power for experimental characterization. Preliminary results of the calculations are in agreement with our measurements showing that Co is buried below a layer of Pt.

Photoemission measurements at UNLV and X-ray absorption and X-ray emission measurements at the ALS were performed on catalyst samples consisting of a nanosized Pt/Co alloy on a C support. These samples were provided by UTC Power. As is exemplarily shown for $Pt_{75}Co_{25}/C$ in Figure 7, our surface-sensitive photoemission measurements (information depth of ~1-3 nm) only show the lines of Pt, C, and O, while no signal from Co can be detected (compare the expected binding energy and line intensity in Figure 7, right, as indicated by the red bars). In contrast, the more bulk-sensitive X-ray emission spectroscopy (XES) spectra (not shown, information depth >100 nm) clearly identify

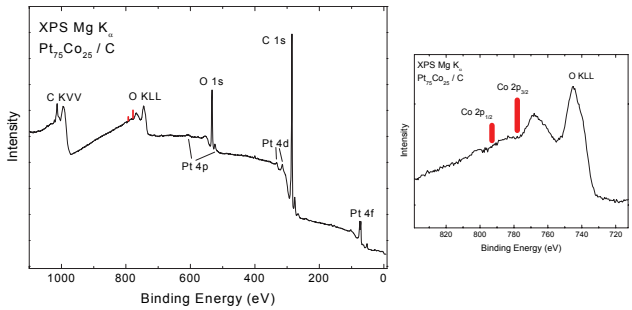

FIGURE 7. XPS Spectra of a $Pt_{75}Co_{25}$/C Powder Sample (The red bars indicate position and intensity of the Co 2p lines for a nominal Pt:Co surface stoichiometry of 3:1.)

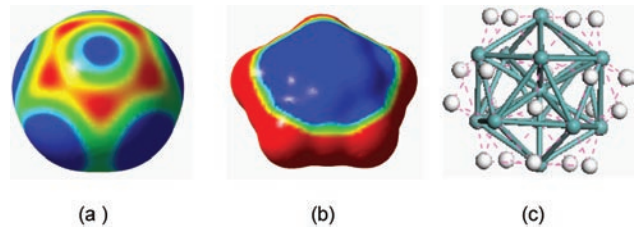

FIGURE 8. Electrostatic Potential Map of (a) Ti_7 and (b) Ti_7H_{20}; (c) Structure of $Ti_{13}H_{20}$

Co emission from these samples. This suggests that the Co atoms in the investigated samples are buried below a layer of Pt and/or C. As mentioned above, this finding has been tentatively confirmed by theoretical calculations.

A thorough analysis of our XES, X-ray absorption spectroscopy (XAS), and XPS spectra reveals the presence of oxidized Pt on some samples, while Co is not oxidized at all. This is an interesting find and will serve as the basis for a complete series of further investigations. Clearly, such information about the oxidation behavior of the catalyst material is one of the key stability issues for fuel cell catalysts, particularly when low-cost alloy catalysts are being employed.

Nanoclusters and Catalysis

Due to the significant interest in Ti as a catalyst in reversible hydrogen storage in complex metal hydrides and also in Ti decorated nanomaterials as potential hydrogen storage systems, we have undertaken a detailed study of the electronic structure and bonding in small Ti clusters. Small titanium clusters up to 15 atoms and the dissociative chemisorption of H_2 on the minimum energy clusters were investigated using DFT under the generalized gradient approximation (GGA). A paper describing our calculations is published in J. Phys. Chem. C (2007). The studies showed strong dependence of chemisorption energy with cluster size. Currently we are looking into the sequential dissociative chemisorption of H_2 on Ti_7 and Ti_{13} clusters which have exceptional stability compared to other Ti_n clusters. Detailed molecular orbital analysis revealed that the reaction processes is driven by charge transfer initially from H to Ti and subsequent back donation from Ti to H leading to more negatively charged H atoms. Furthermore, hydrogen saturation leads to a flattening of the titanium cluster and profound changes in the electrostatic potential surrounding the metal atoms. This is illustrated in Figure 8 (a,b) where the electrostatic potential map of the bare Ti_7 cluster and Ti_7H_{20} are depicted. The most negative region is shown in red and the most positive region is shown in blue. Interestingly, the presence of hydrogen on the cluster seems to accelerate the hydrogen adsorption process.

Studies are in progress on the role of Ti as a catalyst in reversible hydrogen storage in $NaAlH_4$. In particular, we have performed a systematic investigation of the electronic structures, bonding, and growth patterns of nanoclusters of Al-Ti alloys using DFT calculations. The reactions of H_2 with a $TiAl_3$ cluster have been studied at various binding sites and showed that H_2 undergoes dissociation at Ti end or at Ti-Al bond sites, whereas interaction between H_2 and Al is found to be repulsive in nature. We believe our calculations can provide mechanistic insights into the role of Ti in reversible hydrogen storage in complex metal hydrides.

We have also investigated the electronic structures of small clusters of Pd and Pt and explored the growth of small Pt clusters on an α-Al_2O_3 surface. Although electronic structures of subnanoclusters of Pt and Pd have been extensively investigated, their interaction with support materials are not well understood. This work has been accepted for publication in J. Phys. Chem-C. More work is in progress on the chemisorption of H_2, O_2 and CO molecules on Pt clusters deposited on an α-Al_2O_3 surface.

Conclusions and Future Directions

The implementation of a variety of first principles models and simulations has permitted systematic studies of electronic states and energetics of various bonding sites for a variety of materials. This capability permits rapid assessment of performance of different configurations with regard to hydrogen sorption and desorption. The developed theoretical and computational capabilities to predict thermodynamic behavior of materials have been applied to a systematic study of the thermodynamic properties of solid metal hydrides. This study provides a basis for a similar assessment of the thermodynamic behavior of candidate materials for hydrogen storage in practical implementation conditions.

The establishment of capability to acquire laterally integrated and highly localized spectral characterization

of candidate materials provides a detailed understanding of how electronic states change under different configurations and with different inclusive substances. This capability has already identified peculiarity in the way Co is associated with a Pt-Co catalyst surface. It will be applied to experimentally investigate the changes in electronic structure of candidate storage concepts and the bonding energies of hydrogen in different realizations. Finally, the established measurement capabilities using high-brightness synchrotron radiation, in collaboration with developing theoretical capabilities, will permit highly resolved and unparalleled validation of theoretical and computational models.

Molecular dynamics has been applied to the study of a novel carbon-based 3-dimensional nanoframework, establishing its theoretical stability up to 600 K. Methods to synthesize such nanoframeworks have been reported in the literature. The large accessible area characterizing this new class of materials should be favorable for hydrogen storage and the short hydrogen diffusion paths in such nano-sized structures are expected to promote hydrogen release with diffusion coefficients typically higher than in polycrystalline materials. Performance of the designed material in hydrogen storage applications, and modifications to enhance performance are topics of continuing work.

A one-pot synthesis of PANI/Pd has been developed and demonstrated. Hydrogen sorption measurements have been initiated.

Sulfonated polymer thin films have been synthesized and analyzed. Molecular dynamics models were applied to understand the relationship between film flexibility and its molecular structure. Further studies will address proton conductivity.

Computational studies on new light-element and solid metal hydrides will continue. The focus will be to establish a fundamental understanding of the microscopic mechanism for hydrogen adsorption and desorption near ambient conditions. Based on such information, new materials and/or material configurations will be proposed for optimal performance. Collaboration with the experimental component will also continue. The goal is to coordinate the theoretical and experimental efforts to produce both theoretical understanding and experimental realization of new hydrogen storage materials with desirable properties.

We will continue our studies of nanomaterials, using scanning tunneling microscopy and STS to probe local electronic structure. Particular focus will be on SWCNTs, Ti-coated SWCNTs, and SWCNTs (with and without Ti) exposed to molecular or atomic hydrogen at varying temperature. We will study BN-based nanotubes as well. We are pursuing co-adsorption experiments with light alkali and/or alkaline-earth metals to study whether such metals can "pluck" oxygen from the Ti atoms, possibly alleviating rapid formation of TiO and TiO_2. The unique capabilities of the new XES spectrometer at the ALS will be used to study the electronic structure of various nanomaterials (in particular SWCNT, BN-NT) during scheduled beam time in late September 2007.

In close collaboration with our partners at UTC, we will continue to study industrially-relevant CoPt nanoparticle catalyst alloys, in particular the composition and structure of the nanoparticles.

For the mesoscopic polymer/metal composites, our goals for the next year are centered on evaluating the hydrogen sorption and catalysis studies using chemically and electrochemically produced PANI/Pd. From the experimental results we have developed a method for converting Pd/aniline complexes into polymer with Pd(0). This process will be evaluated and optimized. We will continue to evaluate Pd speciation in samples to determine how speciation influences hydrogen sorption/desorption. We have purchased kinetics software for differential scanning calorimeter/thermogravimetric analysis and we plan examining the use of this software and technique in determining the ratio of oxidized Pd in comparison to Pd metal. We will also continue to use thermal analysis on the composite materials to determine how Pd incorporation influences the polymer.

For the development of optimized fuel cell membranes, an evaluation of other membrane properties of the synthesized polyelectrolytes (**1a – 1d**) such as water uptake, hydrolytic stability, thermal stability will be pursued and their results will be submitted for publication in peer-reviewed journals.

FY 2007 Publications/Presentations

Publications

1. Xuezhi Ke and Changfeng Chen, "Thermodynamic functions and pressure-temperature phase diagram of lithium alanates by ab initio calculations", ***Physical Review B***, in press (to appear in June 15, 2007 issue).

2. Archer, David, 'Quantum Mechanical H-H_2 Collisional Cross Section Calculations for Astrophysics' Ph.D. Thesis (2006).

3. C. Zhou, C. Luo, J. Wu, T. J. Dhilip Kumar, N. Balakrishnan, R. C. Forrey and H. Cheng, First principles study of small palladium cluster growth and isomerization, Int. J. Quant. Chem. **107**, 1632 (2007).

4. 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).

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7. E. Kim, T. Pang, W. Utsumi, V. L. Solozhenko, and Y. Zhao, "Cubic phases of BC_2N: A first-principles study," Phys. Rev. B. 75, 184115 (2007).

8. R. Kumar, E. Kim, O. Tschauner, A. Cornelius, M. P. Sulic, and C. M. Jensen, "Pressure-induced structural phase transition in NaAlH4", Phys. Rev. B. 75, 174110 (2007).

Presentations

1. Yi Zhang, Hong Sun, Changfeng Chen, "Ab initio study of H_2 adsorption in graphitic BC_2N", presented at the American Physical Society March Meeting, held in Denver, CO, March 5–9, 2007; abstract number R1,133.

2. Xuezhi Ke, Changfeng Chen, Ole Martin, "Thermodynamic properties of calcium alanate from first-principles calculations", presented at the American Physical Society March Meeting, held in Denver, CO, March 5–9, 2007; abstract number R1.134.

3. Xuezhi Ke and Changfeng Chen, "Thermodynamic properties of $LiAlH_4$ from first-principles calculations", presented at the American Physical Society March Meeting, held in Denver, CO, March 5–9, 2007; abstract number L39.014.

4. Yi Zhang, Hong Sun, and Changfeng Chen, "First-principles study of cubic BC_6N: Structural forms and idealstrength", presented at the American Physical Society March Meeting, held in Denver, CO, March 5–9, 2007; abstract number S23.002.

5. Patricia E. Kalita, Stanslav Sinogeikin, Andrew Cornelius, Kristina E. Lipinska-Kalita, Thomas Hartmann, Xuezhi Ke, and Changfeng Chen, "Investigations of TiH_2, a compound of potential interest for hydrogen storage, up to the megabar region", presented at SMEC 2007 held in Miami Beach, April 15–20, 2007.

6. Balakrishnan Naduvalath, Molecular adsorption and dissociation on transition metal clusters and alloys, presentation to representatives from United Technology Corporation, 03/28/07, UNLV.

7. T. J. Dhilip Kumar, P. F. Weck, and Balakrishnan Naduvalath, Evolution of small Ti clusters and the dissociative chemisorption of H_2 on Ti, APS March Meeting, March 5–9, 2007, Denver, CO.

8. T. J. Dhilip Kumar, C. Zhou, and Balakrishnan Naduvalath, First principles study of adsorption and dissociation of H_2, O_2 , and CO on α-Al_2O_3 (0001) supported Pt-Co alloy, APS March Meeting, March 5–9, 2007, Denver, CO.

9. P. F. Weck, E. Kim, N. Balakrishnan, and H. Cheng, Design of tailored carbon nanostructures for hydrogen storage, APS March Meeting, March 5-9, 2007, Denver, CO.

10. T. J. Dhilip Kumar, C. Zhou, and B. Naduvalath, R. C. Forrey and H. Cheng, First principles study of adsorption and dissociation of H_2, O_2, and CO on Pt_4 and Pt_3Co clusters, DAMOP Meeting, June 5–9, 2007, Calgary, Canada.

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12. E. Kim, D. Stucke, and T. Pang, "Oxidation of Pt (100) surface: *Ab initio* studies", 2007 APS March Meeting, Denver, CO, March 5–9, 2007.

13. E. Kim, "Theoretical study of solid sodium borohydrides under Pressure", MRS Fall meeting, Boston, MA, November 26–28, 2006.

14. E. Kim, "Instability of carbon nanotubes: Molecular-dynamics Simulations", International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA, August 20–25, 2006.

15. P. F. Weck, T.J. Dhilip Kumar, E. Kim, and N. Balakrishnan, "Computational study of hydrogen storage in organometallic compounds", International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA, August 20–25, 2006.

16. C. Heske, FreedomCAR Technical Team Meeting, Detroit, December 2006.

17. C. Heske and B. Naduvalath, DOE Hydrogen Review Meeting, Arlington, VA, May 2007.

18. C. Heske, Rocky Mountain ACS Meeting, Tucson, AZ, October 2006.

19. C. Heske, Seminar Experimentelle Physik II, University of Würzburg, Germany, July 20, 2006.

20. C. Heske, Materials Science and Engineering Department, Stanford University, August 31, 2006.

21. C. Heske, Group seminar, Prof. T. Moustakas, Boston University, November 17, 2006.

22. C. Heske, Physics Department Seminar, Boston University, December 8, 2006.