

IV.G.4 Fundamental Research for Optimization of Hydrogen Storage and Utilization*

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*Congressionally directed project

- 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 (section 3.3.4.2):

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

Fuel Cells barriers (section 3.4.4.2):

- (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.

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 surfaces.
 - Rate coefficients for atomic and molecular hydrogen interactions in thermal and non-thermal populations.

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 the adsorption/desorption processes.
- Structural effects of hydrogen adsorption/desorption in various nanomaterials.
- Storage material states and effects of temperature and pressure.

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

- The stability of a single-wall carbon nano-tube (CNT) was studied using molecular dynamics simulations based on a self-consistent charge density functional binding method for investigating the effects of hydrogen absorption/desorption on nanotube durability.
- Density functional theory (DFT) calculations using pseudopotentials generated from numerical atomic orbitals specially tailored for the study of hydrogen storage with CNTs have been applied for the study of hydrogen storage in Ti-decorated CNTs.
- Established a systematic description of the interlayer stacking and band gap structure of BC_2N preparatory to determination of hydrogen absorption sites, path and barrier descriptions and binding energy in graphitic BC_2N .
- Described the structural and phase changes of BC_2N under external stress to establish possible improvements for hydrogen absorption site selection and mechanical control of hydrogen storage process in BC_2N .
- A theoretical guide wave function has been developed for a hydrogen molecule in an arbitrary cage to understand experimental observations of unusual freedoms of a confined hydrogen molecule.
- Designed and authorized fabrication of a nanodeposition system consisting of an electron beam evaporator, a sputter unit, a plasma enhanced chemical vapor deposition system and a thermal deposition system for the growth of extremely pure carbon nanotubes (CNTs).
- Synthesized and characterized polyaniline palladium composites preparatory to preparing mesoporous templates to provide coating substrates.
- Stress effects on the structure of $NaBH_4$ were studied using ab initio materials models providing theoretical basis for experimental observations of phase changes of $NaBH_4$.
- Demonstrated transition of $NaBH_4$ from cubic to tetragonal structure at about 6 GPa and further transition to orthorhombic structure at about 9 GPa.
- Temperature and pressure induced phase changes have been demonstrated in TiH_2 .
- Initiated fuel cell polymeric materials development by preparing aromatic polyamides of high molecular weight with using optimized relative amounts of additives (pyridine, triphenyl phosphate, $CaCl_2$ and $LiCl_2$) for research and development of cheaper and more durable fuel cell membrane electrode assemblies (MEAs).
- H-H₂ collision calculations have been completed and analysis of these results is underway.
- O-H₂ collision calculations have been completed with possible application of some of these results to hydrogen combustion models.
- Rotational transition cross-sections were computed from recent H₂-H₂ interaction potentials for better understanding of transport and relaxation properties of molecular hydrogen.
- The equipment for inverse photoemission was commissioned in the first months of 2006; a new high-performance electron analyzer (SPECS PHOIBOS150 MCD) was added in May 2006; an ultra-high vacuum scanning probe microscope (Omicron VT AFM XA) was delivered in the first week of June and will be installed and commissioned before this report is submitted; finally, a custom-built atomic hydrogen source has been constructed for loading CNTs and boron-based nanomaterials with atomic hydrogen.
- Synchrotron-based soft x-ray spectroscopy experiments at the Advanced Light Source at Lawrence Berkeley National Laboratory have been performed.
- A 17-node opteron cluster has been procured and fully configured for computational research.

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 interesting for hydrogen storage and for fuel cell applications.

Recent work on nanotubes has studied 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 sp² to sp³ 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.

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 H₂ adsorbed on host matrices including carbon and boron nitride nanotubes, as well as providing a comprehensive data base of H-H₂, H₂-H₂ collisional rate coefficients over a wide range of temperature with thermal and nonthermal populations of H₂. Accurate calculations of catalytic dissociation of H₂ 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 materials for efficient solid state hydrogen storage and permeation.

Results

CNT Structural Stability

The stability of single-walled carbon nano-tubes (CNTs) with different hydrogen coverage conditions was studied. The role played by hydrogen in the disintegration process of CNTs is unraveled through molecular-dynamics simulations based on the self-consistent charge density-functional tight-binding method. The defected nanotube completely recovers its defect-free structure within 0.1 ps at 600 K in the hydrogen-free condition. However, when the dangling bonds of unzipped carbon atoms are saturated by hydrogen atoms, the self-healing process is incomplete. With appropriate coverage of hydrogen, which can convert all the double bonds into single bonds in the carbon nano-tube, the unzipping process proceeds further and results in graphite flakes, as observed experimentally during the purification process. This work is summarized in a manuscript submitted to a peer-reviewed journal. Additionally, density functional theory (DFT) calculations using pseudopotentials generated from numerical atomic orbitals specially tailored for this study have been applied for the study of hydrogen storage in Ti-decorated CNTs.

Structural and Energetic Modeling of B-C-N Materials

Systematic work established structural models for boron-carbon-nitrogen (B-C-N) nanostructures and the computational approaches for energetic and structural simulations. The early studies addressed determination of the equilibrium structural form and electronic properties of a graphitic phase of BC₂N, which is one of the most stable B-C-N structures, before the hydrogen loading. The results provide a systematic description of the interlayer stacking and the electronic band structure with the GW correction (product of the Green's function, G, and the energy, W) for the band gap. These results are reported in a paper entitled "Interlayer Stacking and Nature of the Electronic Band

Gap in Graphitic BC₂N: First-principles Pseudopotential Calculations” that has been published in Physical Review B 73, 193304 (2006). The next step will study hydrogen adsorption in this graphitic BC₂N structure. Emphasis will be on the determination of the adsorption sites, path, barrier and binding energy.

A second study has examined the structural change of the BC₂N phase under external stress and the associated transformation path and energy barrier. These results provide important insights into possible improvements for hydrogen adsorption site selection and the external mechanical control of the hydrogen storage process. A paper on this topic entitled “Ab Initio Structural Identification of High Density Cubic BC₂N” has been published in Physical Review B, 73, 214111 (2006).

Quantum Monte Carlo Simulation of Hydrogen Molecules in Host Matrix

The behavior of a hydrogen molecule in a confined environment such as a cage represented by host matrix is sensitive to the cage shape and dimensions. Recent experimental observations have shown unexpected freedom of a hydrogen molecule inside such a cavity and how the confinement affects the shape of the molecule. A guide wave function for a hydrogen molecule in an arbitrary cage has been constructed and will be used to optimize matrix element shape and size for minimum energy of trapped hydrogen.

Quantum Mechanical Study of H₂ Dissociation and Sticking Probabilities of H on Pt Surface

Rapid progress on these calculations is expected in the coming months as the necessary computing infrastructure and personnel are in place. Density functional theory (DFT) calculations were performed to explore hydrogen storage on carbon nanotubes covered with Ti atoms. Unlike previous studies that employ mostly standard ultrasoft pseudopotential libraries, the DFT calculations make use of pseudopotentials generated from numerical atomic orbitals specially tailored for the study of hydrogen storage with CNTs. Various new pseudopotentials have been developed and tested for transition metals and carbon suited for the study of hydrogen storage. Extensive structural characterization and optimization of Ti-decorated CNTs with hydrogen adsorbed have been performed. These studies directly address the issue of hydrogen storage which is a key focus of the overall project and is an important step toward collaborative work with the experimental effort.

Fundamental Studies of H-H₂ and H₂-H₂ Collision Rates

The bulk of the H-H₂ calculations have been completed. Results are being analyzed and two to three publications are expected come out of this work. Calculations of O+H₂ collisions have also been completed, resulting in a peer-reviewed publication. The H₂-H₂ calculations are in progress. In these calculations, the H₂ molecules are treated as rigid rotors. A paper describing comparison of rotational transition cross-sections computed using two recent H₂-H₂ interaction potentials has been submitted for publication. Extension of the H₂-H₂ calculations to include vibrational motions of the two H₂ molecules is in progress. The calculations will provide important data on transport and relaxation properties of molecular hydrogen.

Nanomaterial Synthesis and Fabrication

Specialized equipment was designed and ordered for the fabrication of high quality carbon nano-tube matrices. The equipment consists of a nanodeposition system, an electron-beam evaporator system and a sputtering unit. In addition, the equipment has a plasma-enhanced chemical vapor deposition component (PECVD) and a thermal deposition system for the growth of carbon nano-tubes. Combining the nanodeposition system together with the carbon nano-tube growth system, the equipment will allow the growth of high quality carbon nano-tube matrices. The equipment is expected to be delivered in September 2006. Preliminary experiments were carried out to incorporate nanoparticles inside alumina matrices by electrophoresis. A specialized apparatus was designed for this process and experiments are currently in progress. Carbon nano-tubes grown on a substrate were obtained from a collaborator to investigate and develop the nano-tube array imaging capabilities at UNLV. While the sample quality was not very good (the nano-tubes were not ordered and there was excessive catalyst material), the in-house scanning electron microscope in the Nanotechnology laboratory did image them and characterize them successfully.

Mesoporous Conductive Polymer Membranes

First year studies of mesoporous conductive nanostructures for hydrogen storage addressed synthesis of the polyaniline (PANI) palladium composites. The first synthetic method was carried out via chemical oxidation of the monomer in the presence of Pd anions (PdCl₆²⁻ and PdCl₄²⁻). This method can be used to produce large quantities of the polymer with good reproducibility. The process is unique in that the chemical oxidant is used to initiate polymerization and provide the metallic Pd that is encapsulated in the

final composite. Chemical polymerization of aniline using this method will be utilized to produce the large quantities of polymer needed to coat mesoporous structures in situ. Currently, the chemical properties of the materials are under study.

In addition to chemical synthesis, the electrochemical synthesis of the PANI/Pd composites using PdCl_6^{2-} and PdCl_4^{2-} was completed. The electrochemical synthesis utilized the normal anion doping of PANI at positive potentials to disperse the Pd anions into the polymer matrix. When the potential is reversed to more negative values the Pd anions reduce at the point of contact in the material producing Pd(0) particles. Although the energy for the reduction of both anions is very similar the processes produce different materials. In the case of PdCl_6^{2-} the polymer becomes more oxidized and evidence for polymer degradation is observed in cyclic voltammetry. Examination of the morphology of the deposits and the composite materials is underway.

Characterization of the chemical properties of the materials requires quantitation of the hydrogen uptake and evolution. An electrochemical quartz crystal microbalance has been acquired to measure the potential mediated hydrogen evolution reaction. A hydrogen generator that can be used to provide a steady-state flow of hydrogen to the materials in gaseous or aqueous phase has also been acquired. The ability to perform hydrogen evolution using thermal gravimetric methods in the gas phase already exists. Finally a method has been developed to determine the catalytic activity of the materials to ensure the hydrogen is optimized versus the gram weight of metal introduced.

Metal Hydrides

One class of possible hydrogen storage materials is the metal hydrides which absorb large amounts of hydrogen. Significant progress has been made in this field by studying adsorption characteristics of the binary and ternary hydrides. The ternary hydrides such as MXH_4 (M= Li,Na, X=Al,B) show sequences of phase changes and large volume collapse under pressure. These ternary hydrides have been successfully synthesized and experiments have shown that NaBH_4 indeed undergoes a structural transition through an intermediate tetragonal phase. This work along with recent Raman measurements is to be presented at an invited talk and paper at the SRMS-5 (Fifth International Conference on Synchrotron Radiation in Materials Science) in August. The work also investigated structural changes in a metal hydride, NaBH_4 , through ab initio calculations. This theoretical study provides a strong support to the experimental findings. X-ray diffraction and neutron scattering patterns indicate that solid NaBH_4 undergoes phase transitions at about 6 GPa from a cubic phase to a

tetragonal phase and about 9 GPa from a tetragonal to an orthorhombic phase. Theoretical lattice constants of cubic-, tetragonal- and orthorhombic phases are in excellent agreement with experiments. A manuscript is in preparation.

Understanding the phase diagram in this compound has been improved and the results, along with neutron diffraction work at high pressure, will be submitted for publication. TiH_2 has been shown to be a catalyst for hydrogen uptake and release in these materials. Temperature and pressure induced phase transitions in TiH_2 have been demonstrated and the results will be presented as a poster and paper at the SRMS-5 conference.

Polymeric Materials for Fuel Cell Applications

During the first year of this subtask, purities of various aromatic diamine monomers were examined by gas chromatograph mass spectrometry (GC-MS). Several diamine monomers that did not have purity over 97% on GC-MS were purified further by recrystallization. The effort has identified selected monomers for the screening of polymerization and optimized the condition of polymerization using diamine monomer 1a and dicarboxylic acid monomer 2a. As shown in Figure 1, various reaction conditions (i.e. the concentration of monomers in N-methylpyrrolidone (NMP) solvent, the relative amounts of additives [pyridine (Py), triphenyl phosphite (TPP), CaCl_2 , and LiCl_2], and reaction time) were optimized from a reference condition to prepare aromatic polyamide of high molecular weight. Currently, the effort is attempting to synthesize a variety of structures of aromatic polyamides based on the optimized conditions. After characterization of their properties using different techniques and postsulfonation reaction, promising polymeric materials for fuel cell application will be identified.

X-ray Spectroscopy of Materials for Hydrogen Storage

During the first project year, the design and construction of a sample holder for solids was completed, allowing the positioning of small solid samples in the target chamber and x,y,z and rotary motion in vacuum. The electrically isolated samples can

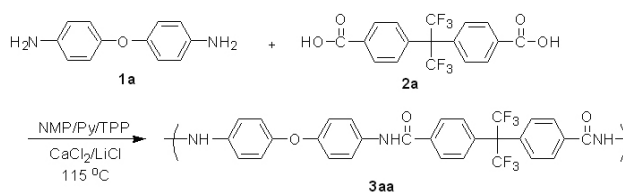


FIGURE 1. Aromatic Polyamide Formulation

be heated and cooled. Preparations are completed to construct 4 new crystal benders, which will expand the range of the current x-ray spectrometer (Cl, 2800 eV) to lower energies in order to measure sulfur (2,300 and 2,460 eV) and to higher energies in order to measure titanium (4,500 eV). The x-ray emission system has been fully tested with chlorine containing compounds, by doing gas phase experiments on chlorofluorocarbons (CFCs). Data acquisition and data analysis software has been developed for planned experiments.

Synchrotron-based soft x-ray spectroscopy experiments on carbon nano-tubes were performed at the Advanced Light Source in Berkeley, CA (LBNL). These experiments successfully provided first results for near-edge x-ray absorption fine structure and soft x-ray emission data near the carbon K-edge of the nanotube samples.

Materials Characterization

Procuring, constructing, and installing the experimental set-ups consumed the first (partial) year. These capabilities are needed for a detailed local structural and spectroscopic characterization of CNTs and boron-based nanostructures and their interaction with hydrogen atoms and molecules. Further effort was made for selecting suitable sources (commercial as well as from basic research partners) for high quality CNTs necessary for performing the planned experiments.

Setting up the instrumentation for the investigation of the electronic structure was completed. In detail, the equipment for inverse photoemission was commissioned in the first months of 2006 and a new high-performance electron analyzer (SPECS PHOIBOS150 MCD) was added in May 2006 (both systems are funded through other projects). The ultra-high vacuum scanning probe microscope (Omicron VT AFM XA), which was procured within the FCAST project, was delivered in the first week of June and is currently being installed and commissioned. Finally, a custom-built atomic hydrogen source has been constructed that will permit the loading of CNTs and boron-based nanomaterials with atomic hydrogen. The needed parts are ordered and will be assembled immediately after receipt.

Single-walled as well as multi-walled CNTs from a commercial vendor have been studied in first test experiments. Among others, transmission electron microscopy (TEM) pictures have been taken from these samples at the UNLV high-resolution TEM facility. One example of a high resolution TEM picture of a multi-wall CNT is show in Figure 2. The research efforts focus on the preparation of nanotube films on surfaces for the local investigation with the scanning probe microscope as well as with laterally integrating electron-spectroscopic probes. These experiments are demonstrating the homogeneity (or

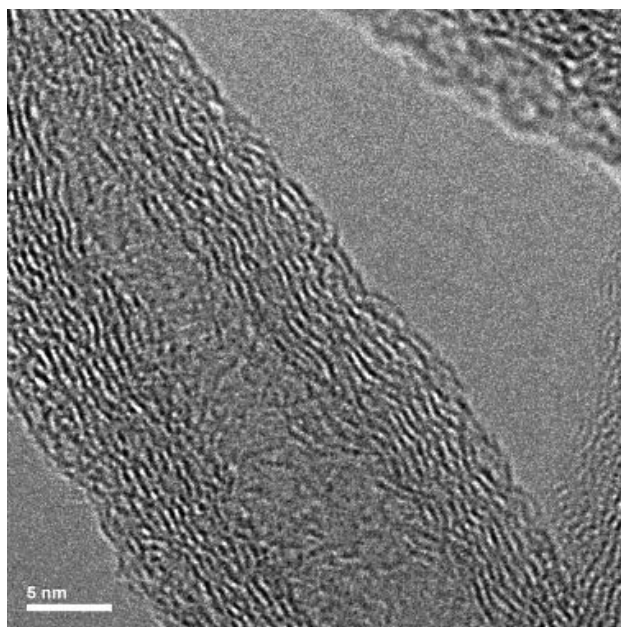


FIGURE 2. High Resolution TEM Image of a Multi-Wall CNT

rather, inhomogeneity) of commercially available samples. Purity and homogeneity are expected to be key parameters for the understanding of the real-world effectiveness of carbon nanotubes for hydrogen storage applications.

Conclusions and Future Directions

A framework of coordinated theoretical and experimental investigation of the physics and chemistry of hydrogen storage concepts has been implemented. Two novel polymeric materials are under development, one for advanced fuel cell applications and the other for hydrogen storage applications. Unique materials characterization capabilities have been, and are being established for use by this and other activities in hydrogen storage and fuel cell investigations. High purity storage matrix fabrication capabilities are being established. Fundamental studies of specific molecular-level aspects of hydrogen storage in nanomaterials and metal hydrides are under way.

FY 2006 Publications/Presentations

1. P. F. Weck, N. Balakrishnan, J. Brandão, C. Rosa, and W. Wang, Dynamics of the $O^{(3P)}+H_2$ reaction at low temperatures: comparison of quasiclassical trajectory with quantum scattering calculations, *J. Chem. Phys.* 124, 074308 (2006).
2. T. G. Lee, N. Balakrishnan, R. C. Forrey, P. C. Stancil, D. R. Schultz, and G. J. Ferland, State-to-state rotational transitions in H_2-H_2 collisions at low temperatures, *J. Chem. Phys.* (in press).

3. Z. C. Pan, H. Sun, C. F. Chen, Interlayer stacking and nature of the electronic band gap in graphitic BC₂N: First-principles pseudopotential calculations, *Physical Review B* 73, 193304 (2006).
4. Z. C. Pan, H. Sun, C. F. Chen, Ab initio structural identification of high density cubic BC₂N, *Physical Review B* 73, 214111 (2006).
5. T. Pang, "An Introduction to Computational Physics, 2nd Edition," (Cambridge University Press, Cambridge, UK, 2006).
6. H. Ma and T. Pang, "Path-Integral Quantum Monte Carlo Study of a Mixture of Bose-Einstein condensates," *Phys. Lett. A.* 351, 92-96 (2006).
7. B. Zygelman, "Spin Changing Collisions of Hydrogen", proceedings of the NASA-UNLV Workshop on Laboratory Astrophysics.
8. A.L. Cornelius and R.S. Kumar, "Structural Transitions in Ternary Borohydrides: Possible Hydrogen Storage Candidates." To appear in the Proceeding of SRMS-5 Conference.
9. P.E. Kalita, A.L. Cornelius, H. Peter Liermann, W. Yang, "Synchrotron-Based, Energy Dispersive X-Ray Diffraction Study of TiH₂." To appear in the Proceeding of SRMS-5 Conference.