Hydrogen Fuel Cells and Storage Technology Project at UNLV

Clemens Heske (lead-PI Experiment)
Balakrishnan Naduvalath (lead-PI Theory)
Department of Chemistry,
University of Nevada, Las Vegas (UNLV)

May 17, 2006

This presentation does not contain any proprietary or confidential information

Project ID # ST12

Overview

Timeline

- Start – Sept 2005
- End – Sept 2006
- 66% Complete

Budget

- Total project funding
  - DOE - $2,976K
  - UNLV -$ 744K
- Funding in FY05: $3,720,000
- Funding in FY06: $4,207,500
  ($3,366K Federal; $841,500 UNLV)

Barriers

- Barriers

Primary:

M. Hydrogen Capacity and Reversibility

N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Secondary:

A. Cost
B. Weight and Volume
C. Efficiency
D. Durability
E. Refueling Time

Partners

– 12 Subtasks @ UNLV

Objective

Create a framework for interdisciplinary academic research that combines Theory and Experiment to address specific fundamental aspects of hydrogen storage and utilization

Approach

- Establish new infrastructure (Computer Cluster, Experimental Stations, etc.) to perform integrated interdisciplinary studies on Hydrogen Storage (and Fuel Cells)

- Perform closely-coupled theoretical and experimental investigations of
  - hydrogen adsorption/desorption in various matrices to establish a solid fundamental base for optimal storage concepts
  - the electronic structure of metal hydrides, nanomaterials (C, B, N), metal adatoms, and adsorbed hydrogen molecules/atoms
  - Fuel cell membranes and catalytic materials

The Team at UNLV

Experiment

Task #1: C. Bae – Chemistry[2]
Sulfonated Polyamides for Fuel Cell Membranes

Task #3: A. Cornelius – Physics[1]
High-pressure Spectroscopy

Task #4: B. Das - Elect. Engineering[1]
Nanomaterial Fabrication

Task #5: D. Hatchett – Chemistry[1,2]
Mesoporous Nanostructures

Task #6: C. Heske – Chemistry[1]
Nanospectroscopy

Task #11: W. Stolte, O. Hemmers, D. Lindle – Chemistry[1]
X-ray Spectroscopy

Theory

Task #2: C. Chen – Physics[1]
First-principles studies of carbon and boron nitride nanostructures

Task #7: E. Kim – Physics[1]
Study of H_2 Adsorption and Desorption in/on Nanotubes

Task #8: S. Lepp – Physics, B. Naduvalath – Chemistry[3]
H-H_2, H_2-H_2 Collisional Studies

Task #9: B. Naduvalath – Chemistry[2,3]
H_2 Catalysis on Metal Surfaces

Task #10: T. Pang - Physics[1]
Quantum Monte Carlo Study of H_2 in a Host Matrix

Task #12: B. Zygelman – Physics[1]
External Field Control of H_2 in Nanostructures

[1] Primarily Hydrogen Storage
[2] Primarily Fuel Cell
[3] Primarily Fund. Hydrogen Interactions

Integration of Theoretical and Experimental Approaches in FCAST

Preparation

Preparation of Mesoporous Conductive Polymer/Pd Nanostructures [PI: D. Hatchett]

Novel materials for fuel cell membranes [PI: C. Bae]

Preparation and modification of nanomaterials Using wet-chemical and vapor-phase routes [PI: B. Das]

Electronic Structure

First-principles Study of Carbon and Boron Nitride Nanostructures [PI: Ch. Chen]

Hydrogen absorption/adsorption in/on carbon nanotubes [PI: E. Kim]

Quantum Monte Carlo: H_2 in a nanomaterial host matrix [PI: T. Pang]

Electronic Structure

Laterally integrating electron spectroscopy and locally resolved electronic structure [PI: C. Heske]

Hard X-ray Raman Scattering at high pressures and temperatures using high-brilliance synchrotron radiation at APS (Argonne) [PI: A Cornelius]

Soft X-ray absorption and emission spectroscopy using high-brilliance synchrotron radiation at ALS (Berkeley) [PI: W. Stolte]

Fundamentals

H-H_2 and H_2-H_2 collision rates [PIs: S. Lepp, B. Naduvalath]

External field control of hydrogen confined in nanostructures [PI: B. Zygelman]

H_2 catalysis on metal surfaces [PI: B. Naduvalath]

Central Themes of FCAST

Quantify and understand hydrogen bonding (specific capacity):

- Bottom-up approach – fundamental studies in Theory and Experiment

Storage materials:

- C-B-N nanomaterials
- Metal/chemical hydrides (e.g., $NaBH_4$, Ti-H_2)
- Mesoporous polymer/metal nanostructures

Storage conditions:

- Variable temperature
- Variable ambient pressure (ultra-high vacuum to >30 GPa)
- Atomic and molecular hydrogen

Fundamental modeling:

- Total energy calculations, electronic structure, bonding
- Dynamics/kinetics (e.g., adsorption and desorption processes, MC simulations of confined hydrogen)

Fuel cell membranes and catalysis:

- Chemical, thermal, mechanical stability
- Understand catalysis of hydrogen dissociation on various metal surfaces

Nanomaterial Matrix Fabrication

Biswajit Das, Electrical and Computer Engineering,
UNLV Nanotechnology Lab

Objective: to investigate and develop nanomaterial matrices for the effective storage of hydrogen

Approaches:

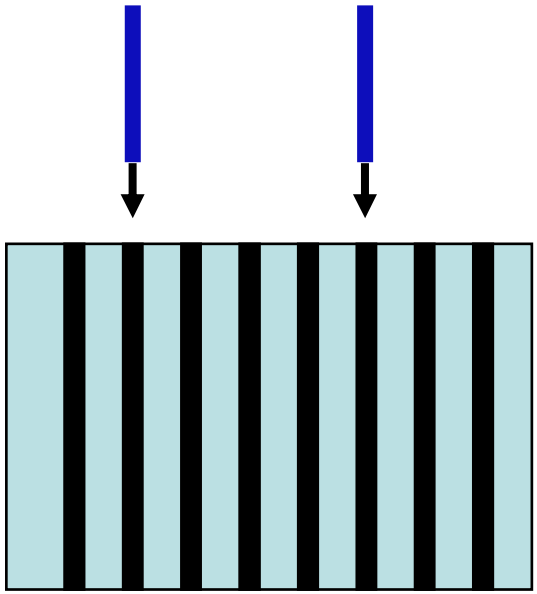
- Chemical/Electrochemical Technique
- Vacuum Synthesis Approach

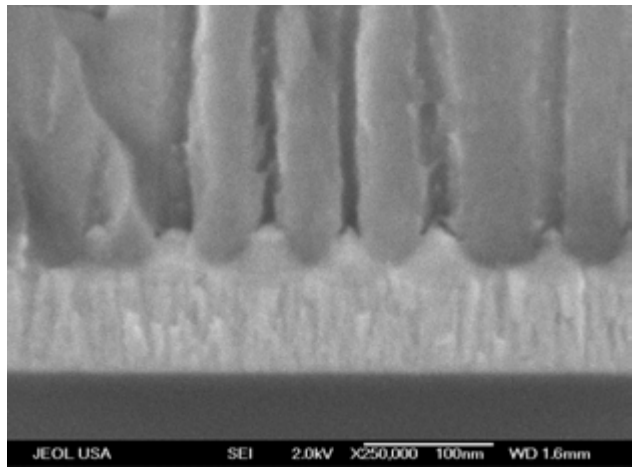
Material Systems of Interest:

Solid matrices of C and BN nanotubes

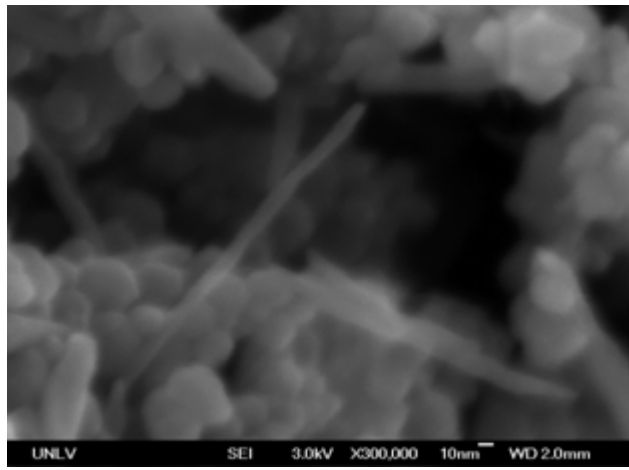
Electrochemical Approach:

Electrophoretically incorporate nanotubes inside a solid matrix





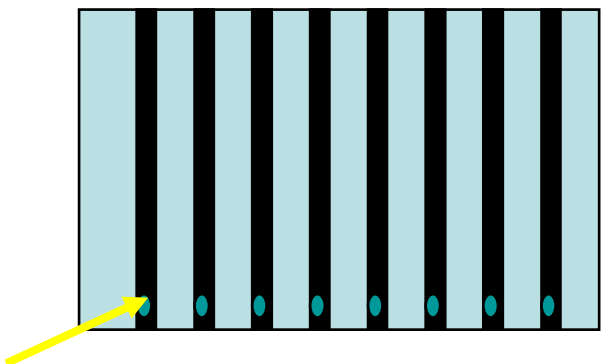
Anodized alumina is currently being used as the solid matrix

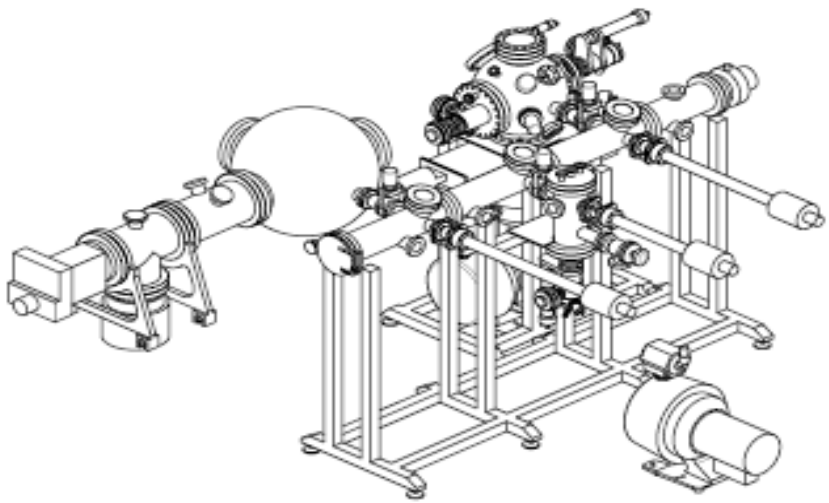


Carbon Nanotubes currently under consideration

Vacuum Synthesis Approach:

Synthesize CNT inside the matrix





Study of hydrogen absorption/adsorption in/on carbon nanotubes

Eunja Kim, Physics

Density functional calculations

•Investigate absorption and adsorption sites inside/outside carbon nanotubes (CNTs):

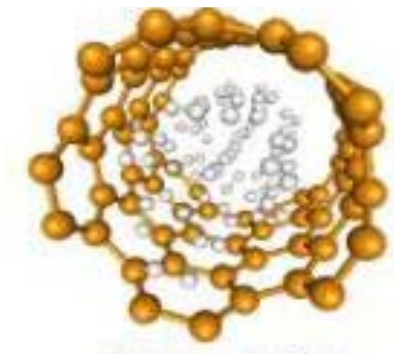
•Verify reactions of hydrogens with CNTs

- Bonding characters of CNTs
- Electronic density of states

• Estimate H storage capacity

•Systematic study on the relationship between diameter of the CNTs and H capacity

CNT



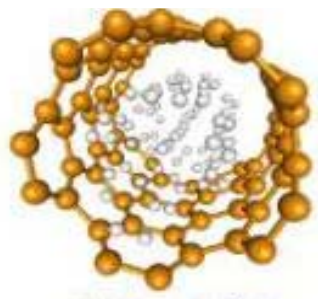
CNT + H

Propose effective methods to improve the storage capacity!!!

Car-Parrinello molecular-dynamics method

Computational details

- Troullier-Martins pseudo-potentials for C atoms and H atoms
- Local density approximation
- Supercells for nanotubes
- Plane waves basis sets
- Kinetic energy cutoff = 60 Ry



Total energy calculations

- Electronic structure (DOS)
- Charge density
- Band structure
- Cohesive energy
- Defect properties
- Vibrational properties
- Structural properties
- Equilibrium geometry
- Absorption and adsorption

Quantum molecular dynamics simulations

At 600 K, with saturation of dangling bonds with hydrogen atoms

- Hydrogen prevents the zipping of nanotube by steric hindrance
- Further unzipping is prevented by strong C-C bonds of the nanotube
- Additional hydrogen may enhance the unzipping process

Hydrogen Storage at Mesoporous Conductive Polymer/Pd Nanostructures

David Hatchett, Chemistry

Polyaniline/Pt and Pd Composites:

- Chemical synthesis involving the direct and spontaneous oxidation of aniline and 4-Aminodiphenylamine using $PtCl_6^{2-}$ and $PtCl_4^{2-}$ (or $PdCl_6^{2-}$ and $PdCl_4^{2-}$)

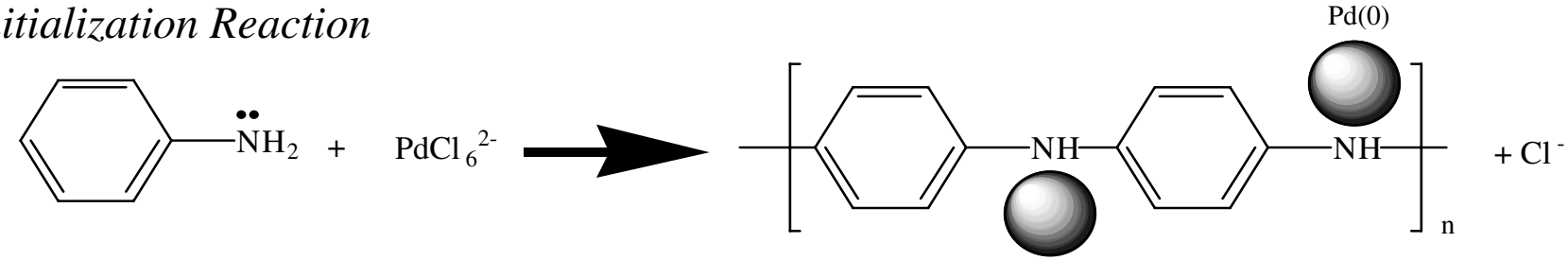
- Electrochemical synthesis of polyaniline (PANI)/Pt (or Pd) composites:
  - Electrodeposition of Pt or Pd into an *a priori* electrochemically prepared PANI film
  - Spontaneous deposition of Pt or Pd into an *a priori* electrochemically prepared PANI film

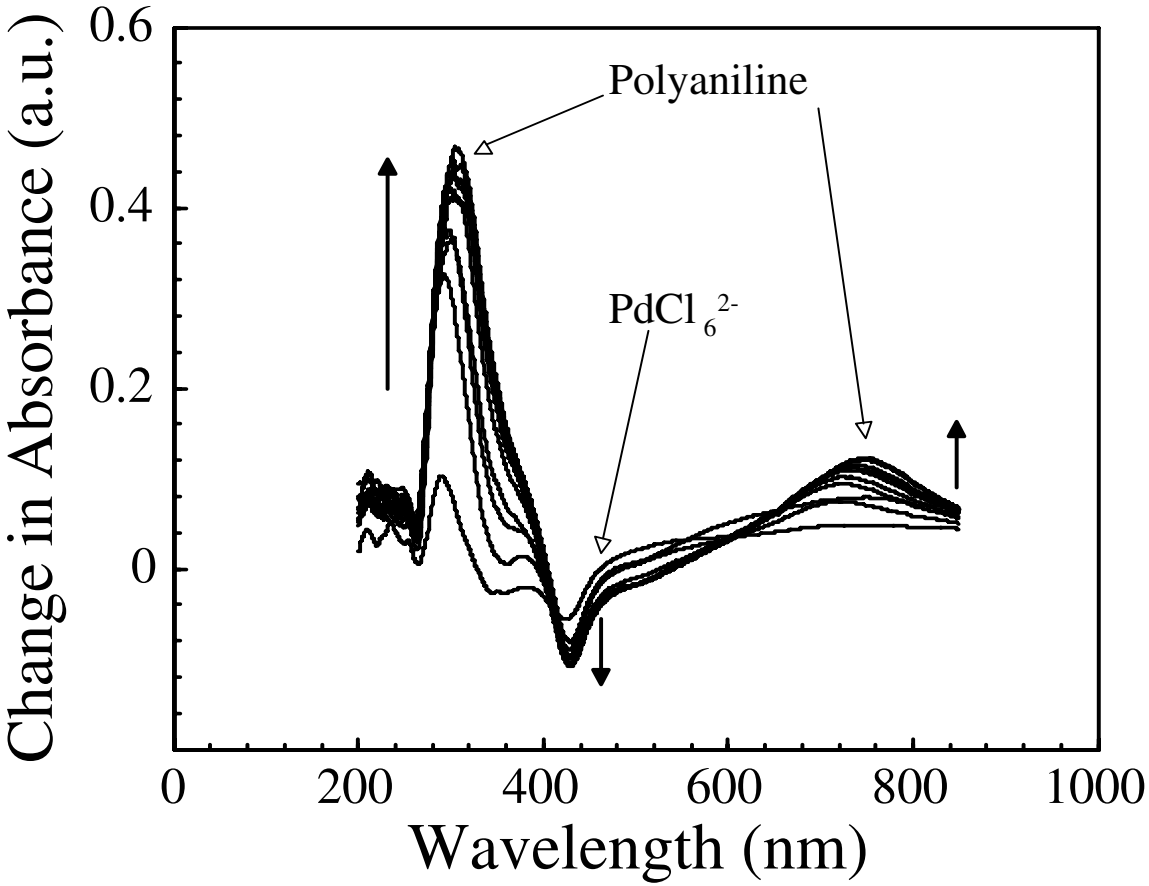
- Finding: the method of metal incorporation influences the level of activity of these composites

- Mesoporous substrates will be used to increase the electroactive surface areas of the polymer and metal surfaces to enhance storage capabilities

In-Situ UV/Vis of Polyaniline/Pd Synthesis: H2 Storage Materials?

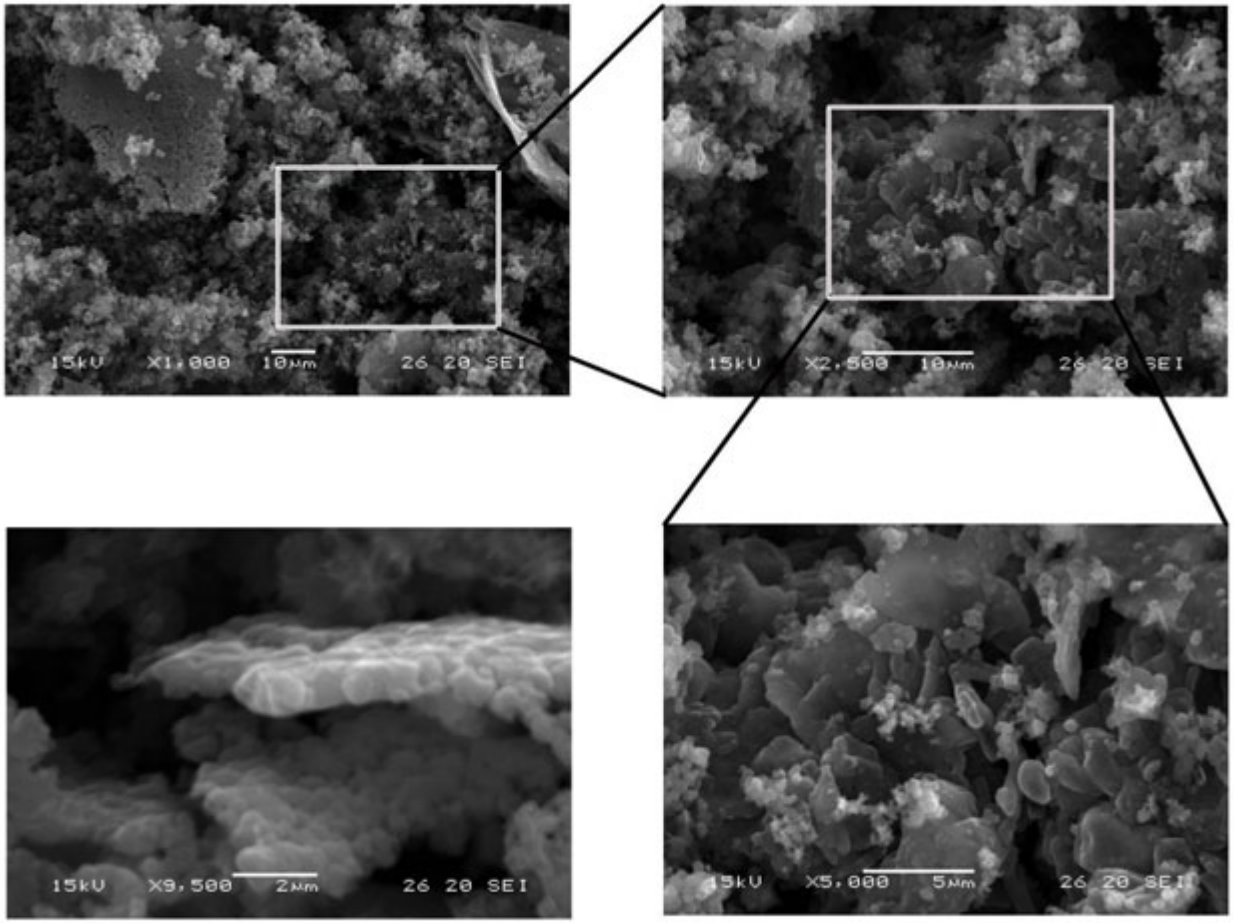
Polymer Initialization Reaction





- **Pd(IV) initializes the oxidation of aniline to Polyaniline**
- **Pd(IV) is reduced to Pd(0) in the process**
- **Emergence of polymer and Pd depletion observed**
- **Colloidal palladium is encapsulated by emerging polymer**

SEM: Chemically Synthesized Polyaniline/Pd Composites



- Polyaniline (darker)
- Pd (lighter)
- Bulk chemical synthesis of gram quantities of PANI/Pd possible
- Built in porosity for H2 uptake
- Pd encapsulated by polymer limits surface fouling

Properties of Potential Candidates for Hydrogen Storage at Elevated Temperatures and Pressures

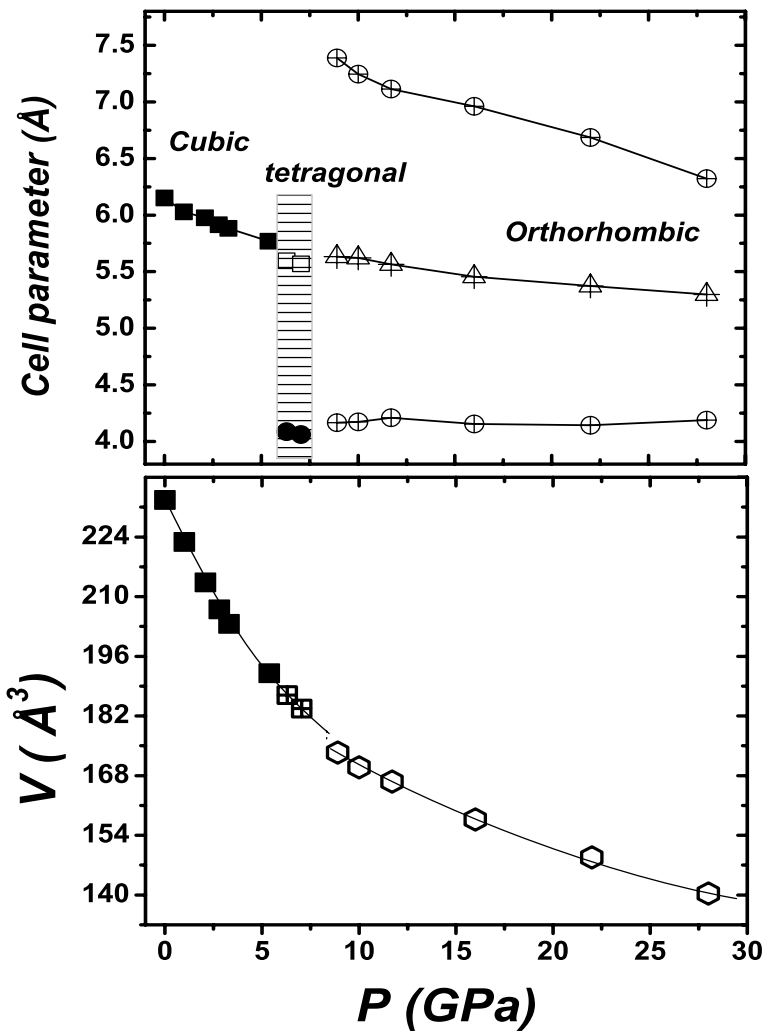
A. Cornelius, O. Tschauner, R. Kumar, Physics

- Study bonding properties of potential H storage materials and catalysts with hard X-rays
  - Carbon nanotubes
  - Metal hydrides

- Working with theorists to understand bonding in these materials

Structure of $NaBH_4$ at High Pressure

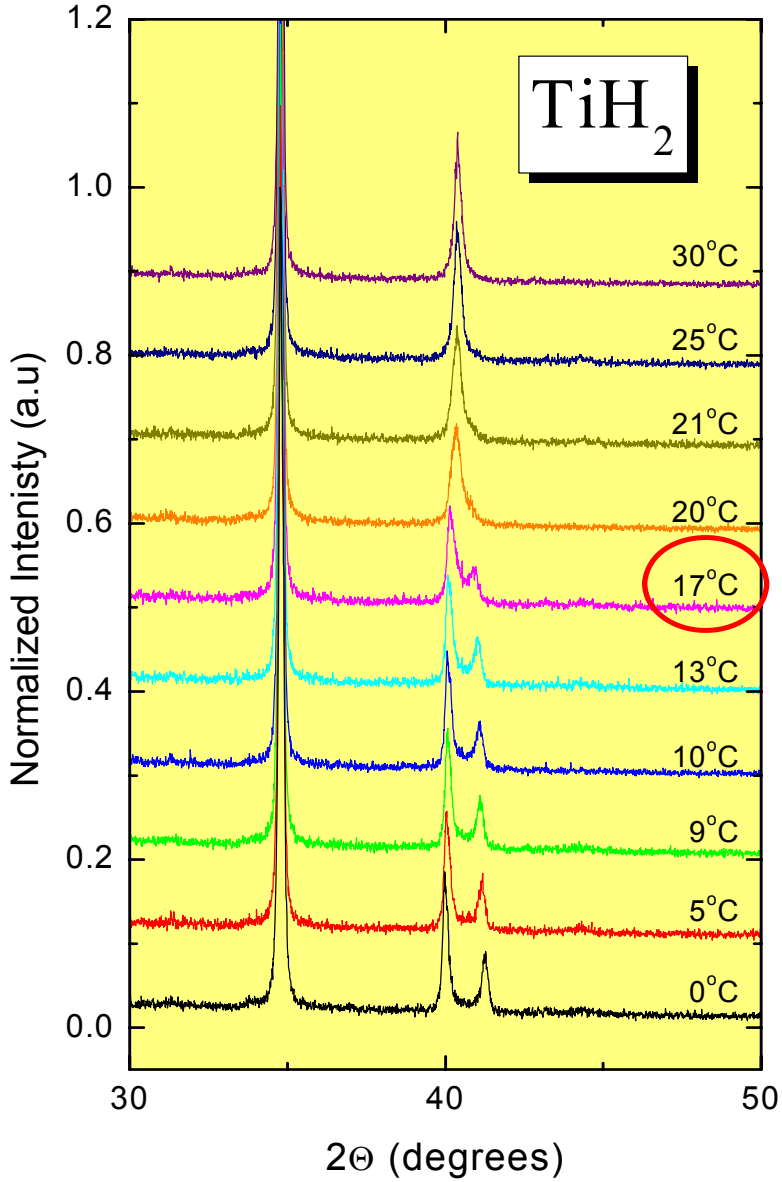
Kumar and Cornelius
Appl. Phys. Lett. 87, 261916 (2005)



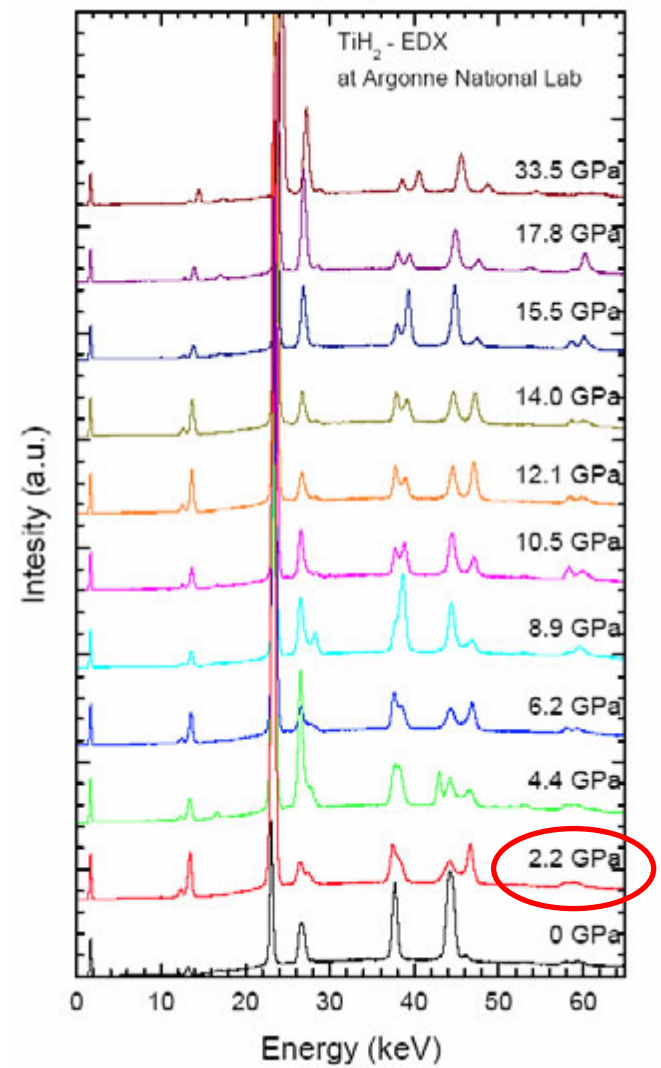
- These compounds contain a very high percentage by weight of hydrogen
- Critical to understand hydrogen uptake and release
  - Need to understand bonding properties
- Pressure modifies interactions between atoms
  - Changes in bonding lead to changes in arrangement of atoms
  - Leads to a better understanding of the way hydrogen bonds in various materials
  - Allows experimentalists ***and*** theorists to look for "better" candidates for hydrogen storage materials
  - Allows a critical test for calculations

Phase Transitions in TiH_2

Kalita *et al.*



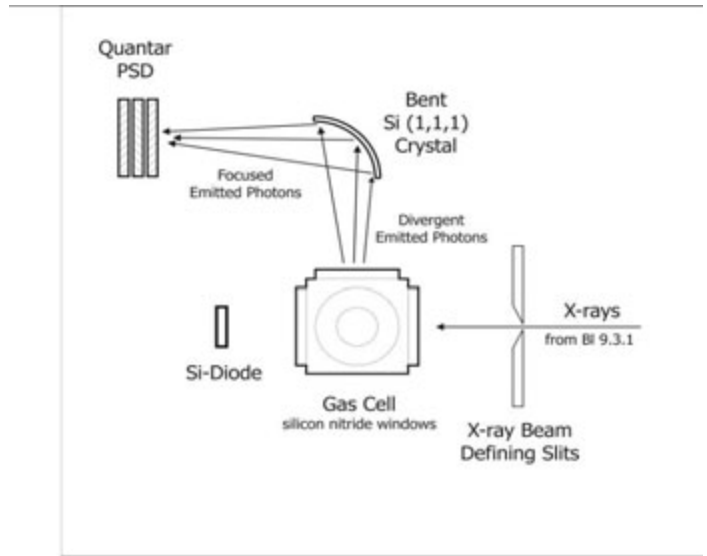
- This material used as a catalyst for hydrogen uptake/release in $NaBH_4$
- Phase transition from cubic to tetragonal as a function of temperature and pressure

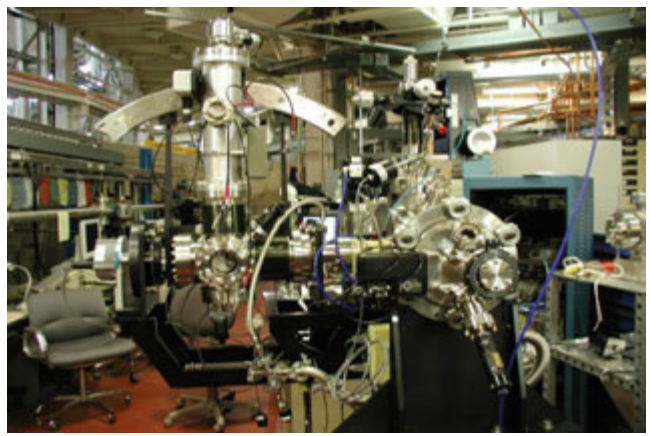


Soft X-ray Spectroscopy of Materials for Hydrogen Storage

Wayne Stolte, Oliver Hemmers, Dennis Lindle, Chemistry

- X-ray emission and absorption spectroscopy probe the electronic structure of occupied and unoccupied electronic states
- The methods are applicable to solids, liquids, and gases
- The obtained partial density-of-states can be directly compared to Theory
- X-ray emission spectroscopy requires high flux → experiments are performed at the ALS, a 3rd Generation Synchrotron light source
- Synchrotron radiation also allows resonant excitation to probe specific resonances and functional groups





The X-ray Emission Spectrometer

Hydrogen storage in B-C-N nanostructures I: Ab initio search for suitable materials

Changfeng Chen, Physics

Research Plan

- Ab initio structural and electronic calculations on nanostructures (tubes, clusters, sheets, etc.) beyond the carbon system
- Determination of important parameters for hydrogen storage, such as binding energy, adsorption sites, path and barrier

Work Progress

- Implementation and testing of computation codes completed
- Structural and electronic properties of B-C-N nanostructures obtained; further calculations in progress

Hydrogen storage in B-C-N nanostructures II: Ab initio material characterization

Research Plan

- Ab initio calculation of density of states, band gap and electronic excitations to characterize materials before and after hydrogen adsorption
- Development and implementation of advanced computational techniques
- Close collaboration with experimental groups within the FCAST.

Work Progress

- Implemented the accurate GW method for determining the band gap
- Studied possible development of more accurate calculations of electronic excitations for a direct comparison with spectroscopy measurements

Hydrogen Molecules in a Solid Matrix: A Quantum Monte Carlo Study

Tao Pang, Physics

- Diffusion Quantum Monte Carlo Simulation
  One of the best schemes for accurate calculations of energy, structure, and dynamics of a small system

- Hydrogen Molecule in Confinement
  A starting point for analyzing the behavior of the electrons in a hydrogen molecule under the confinement potential provided by a typical solid matrix

- Ab initio potential
  The confinement potential of the host matrix can be obtained from first principles methods (Density Functional Theory)

- Interaction between hydrogen molecules
  Investigation of the interaction effect is crucial in learning the weight percentage of hydrogen storage for a given host matrix

Fundamental Studies of Hydrogen in Materials

Bernard Zygelman, Physics

- External field control of hydrogen adsorbed on and inside nanostructures
- Using sophisticated quantum codes, GAMESS & Siesta packages for structure. Dynamics package written by PI
- Comparison with results of calculations with experiment, e.g., spectroscopy results

Fundamental Studies of Hydrogen in Materials

B. Zygelman, Dept. of Physics, UNLV

- Novel applications involving **external field control of nanostructures**:
  - photo-induced currents in heteropolar nanotubes
    [P. Kral et al., Phys. Rev. Lett. 85, 1512 (2000)]
  - control of catalytic activity in nanotube “ropes” excited by infrared light
    [P. Kral, Chem. Phys. Lett. 382 399, (2003)]
  - laser atomic pump for atomic transport through carbon nanotubes
    [P. Kral et al., Phys. Rev. Lett. 82, 5373 (1999)]
  - nanoscale processing by adaptive laser pulses
    [P. Kral, Phys. Rev. B 66, 241401-1 (2002)]
- Using sophisticated quantum codes: the GAMESS & SIESTA packages for structure, and a dynamics package written by the PI
- We will develop a capability for the fundamental study of hydrogen in nanostructures including laser assisted adsorption and desorption
  [D.N. Denzler et al., J. Phys. Chem. B 108, 14503 (2004)]
- Comparison of calculations with experimental measurements

Local spectroscopy of nanomaterials for Hydrogen storage

Clemens Heske, Chemistry

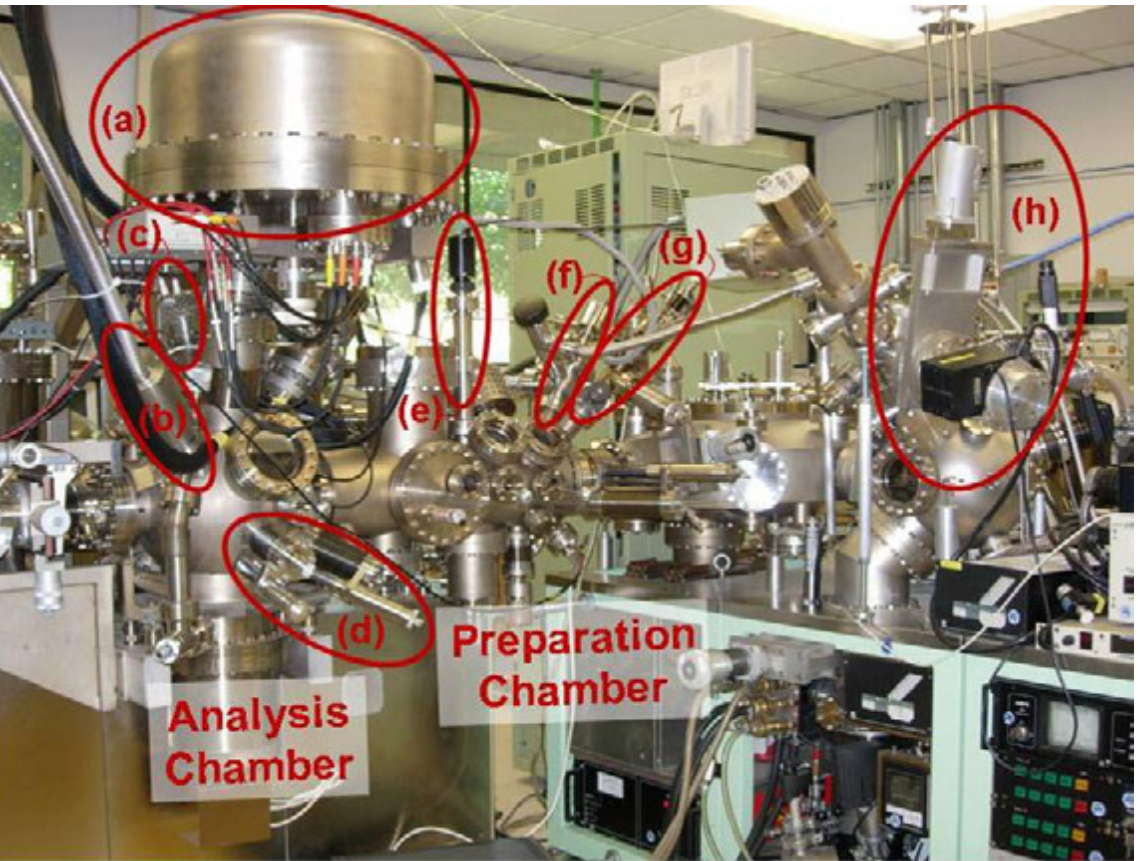
- Combine existing four-chamber ultra-high vacuum system and its unique spectroscopic capabilities with variable-temperature scanning probe microscopy and spectroscopy

Existing:	New:
X-ray photoelectron spectroscopy (XPS)	Scanning Tunneling Microscopy (STM)
UV photoelectron spectroscopy (UPS)	Atomic Force Microscopy (AFM)
Auger electron spectroscopy (AES)	Scanning Tunneling Spectroscopy (STS)
Inverse Photoelectron Spectroscopy (IPES)	Kelvin Probe Force Microscopy (KPFM)

- Determine the electronic structure of
  - Nanomaterials
  - Metal adsorbate/nanomaterial systems
  - H_2 adsorbate/metal adsorbate/nanomaterial systems

- Experimental outcome:
  Valence and conduction band structure, work function, bonding orbitals, geometric structure, …, *on both a laterally integrated and a local scale*

Existing Surface/Interface Analysis and Modification System at UNLV



The Leading UHV STM and AFM Technology

25 K - 1500 K
Beam Deflection AFM
Needle - Sensor AFM
True pA STM and Spectroscopy
In - situ Evaporation Capability
Optimal dI/dV Spectroscopy

New: Variable Temperature Scanning Probe Microscope: STM, AFM, STS, KPFM (expected in May 2006)

Quantum mechanical study of H_2 Dissociation and Sticking Probabilities of H on Pt Surfaces

Balakrishnan Naduvalath, UNLV Chemistry

Project Goal

Perform fundamental theoretical investigations of H_2 dissociation on metal surfaces. Dissociation of H_2 on Pt or other catalytic surfaces is a key step in hydrogen fuel cells.

Program

- Carry out fundamental studies of Pt-H/H_2 &Ti-H/H_2 interaction and adsorption/desorption studies of H/H_2 on Pt & Ti surfaces

- Experiment: Studies on Titanium hydride-doped nanotubes are being carried out (Task 3)

- *Graphene nanostructures as tunable storage media for molecular hydrogen (PNAS, July 2005)* - up to 6.5 wt % of H_2 can be stored under reasonable conditions - Importance of more accurate description of Carbon-H_2 interaction

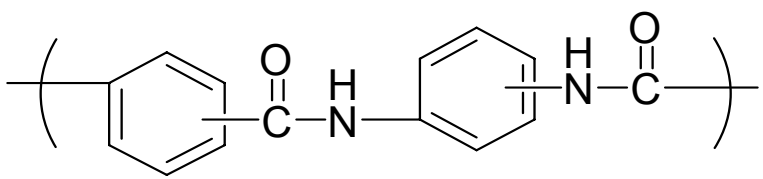
- We are developing/testing computer codes that can model the above systems

Development of Sulfonated Polyamides for Fuel Cell Membrane Materials

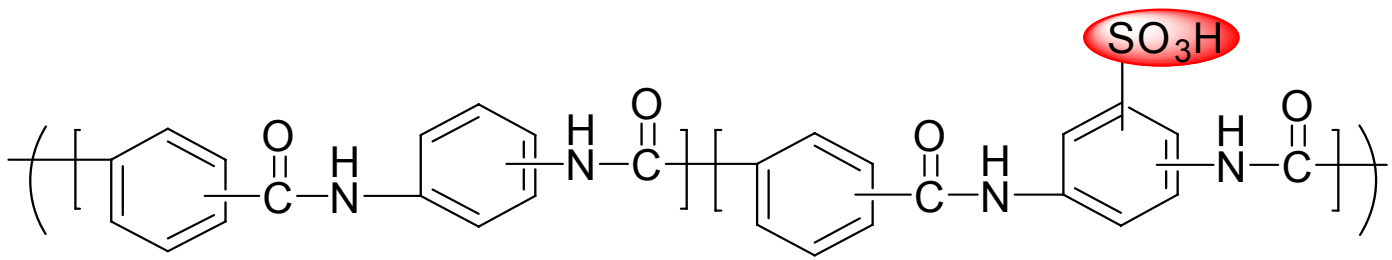
Chulsung Bae, Chemistry

New Proton Exchange Membranes for Fuel Cells

Need better proton exchange membranes (U.S. Department of Energy, 2005)
Current membranes do not meet requirements for commercial fuel cell vehicles

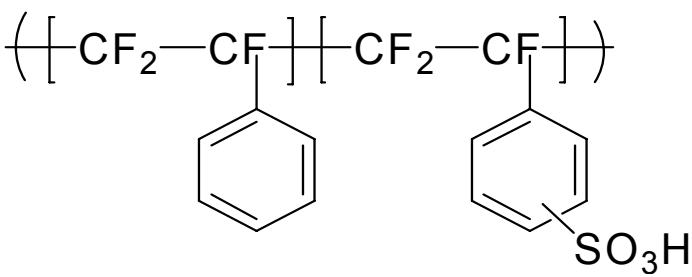


Products of Du Pont (Kevlar, Nomex)
Superior heat resistance (T_m > 400 °C)
Stronger than steel at 1/5 weight
Used in bullet-proof vests

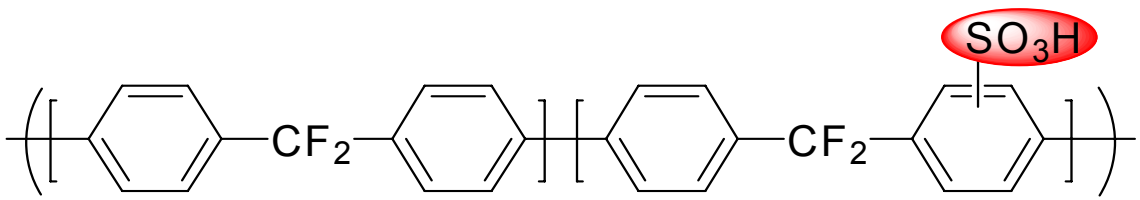


Sulfonated aromatic polyamides
New proton exchange membrane with excellent thermal, mechanical stability

New Proton Exchange Membranes for Fuel Cells



Aromatic side-chain polymers
BAM3G, Ballard Power Systems (Canada)
Currently the best proton exchange membrane for fuel cell vehicles
Fleet fuel cell buses in Vancouver



Partially fluorinated aromatic main-chain polymers
Excellent chemical, thermal, mechanical stability
Better performance than BAM3G in fuel cell applications

Fundamental Studies of H-H_2, H_2-H_2 and O-H_2 Collisions

Steven Lepp, Physics; Balakrishnan Naduvalath, Chemistry

- Detailed understanding of H-H_2 and H_2-H_2 collisions are important in modeling hydrogen combustion process and H/H_2 adsorbed on various matrices
- Quantum mechanical calculations of elastic and inelastic collisional rates will be carried out for both systems
- Test accuracy of the best available interaction potentials for these systems
- Rate constants for $O+H_2$ collisions with thermal and non-thermal populations of H_2 will be computed. Results will be of interest in hydrogen combustion processes.
- Calculations for all these systems are ongoing

Technical Accomplishments/ Progress/Results

- Procurement of infrastructure for project (Computer Cluster, Front-End Computers, Scanning Probe Microscope, Synchrotron Endstation Equipment, …)
- Search/hiring of personnel on all levels: undergraduate students, graduate students, post-docs, Assistant Research Professors, Computer technician
- Commence work in all subtasks
- Preparation of technical paper on stability of hydrogenated CNTs (Task #7)
- Observed P and T effects in metal hydride materials (Task #3)
- Formulation of PANI/Pd composites (Task #5)

Future Work

- Project has recently started (Jan. 06)
- Continue procurement, installation, and commissioning of infrastructure
- Continue implementation of computational codes
- Perform calculations/experiments in all subtasks

Summary

New project:

- Fundamental studies of specific molecular-level aspects of hydrogen storage in nanomaterials and metal hydrides

- Integrated project with unique interaction between Theory and Experiment in a total of twelve subtasks

- Extension of existing infrastructure to perform state-of-the-art calculations, nanomaterial fabrication, and analysis

- Establishment of a network within UNLV and with external research efforts

- Long-term goal: determine the maximal achievable specific storage capacity of a variety of materials and concepts

Publications and Presentations

Presentations:

"Hydrogen Fuel Cells and Storage Technology",
FreedomCAR Initiative, Nov. 10, 2005 (C. Heske)

"X-ray spectroscopy of buried things: interfaces, liquids, and dirty powders",
Stanford Synchrotron Radiation Lab, Feb. 27, 2006 (C. Heske)

"Hydrogen Fuel Cells and Storage Technology",
FORD Motor Company, Mar. 29, 2006 (C. Heske)

Critical Assumptions and Issues

- Chemisorptive Hydrogen bonding can be understood on the basis of the electronic structure
- Close interaction between Experiment and Theory produces synergy effects
- Unique combination of expertise and infrastructure will allow novel insights into Hydrogen storage