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Hydrogen Fuel Cells and Storage Technology (FCAST) Project

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Hydrogen Fuel Cells and Storage Technology (FCAST) Project

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Project manager: Robert F. D. Perret
UNLV Research Foundation

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FCAST partners

UNLV Experiment

• Chulsung Bae – Chemistry
• Andrew Cornelius – Physics
• B.J. Das - Electrical Engineering
• David Hatchett – Chemistry
• Clemens Heske – Chemistry
• Wayne Stolte, Oliver Hemmers, Dennis Lindle – Chemistry

UNLV Theory

• Changfeng Chen – Physics
• Eunja Kim – Physics
• Steven Lepp – Physics
• Bala Naduvalath – Chemistry
• Tao Pang – Physics
• Bernard Zygelman – Physics

External Partners

• United Technologies (UTC) Power
• Rice University
• Lawrence Berkeley National Lab
• Air Products
• Hahn-Meitner-Institute, Berlin
• Shanghai Jiatong University
• Penn State
Why Hydrogen Economy?
Why Hydrogen Economy?

- We need a new fuel! (sooner or later)
Why Hydrogen Economy?

- We need a new fuel! (sooner or later)
  - This could be:
    - Biodiesel
    - Hydrogen
    - Electricity
    - Uranium
    - ...
What would a Hydrogen Economy need?

- Hydrogen Production
- Hydrogen Storage
- Hydrogen Delivery
- Hydrogen Consumption
What would a Hydrogen Economy need?

- **Hydrogen Production**
  - Solar (thermal, photoelectrochemical)
  - Nuclear
  - Currently: natural gas reforming
- **Hydrogen Storage**
  - Nanomaterials, Metal Hydrides, Chemical Hydrides
- **Hydrogen Delivery**
  - Pipelines, Trucks, Tanks, ...
- **Hydrogen Consumption**
  - Fuel Cells, Internal Combustion Engine
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Objectives of FCAST

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

• Collaborate closely with external partners
Approach

Task 1: Theory and Experiment of Nanomaterials for Storage Applications
(New Materials, Hydrogen Uptake, Local Electronic Structure, Adsorption Energies and Geometries, …)

Task 2: Metal Hydrides (Structure, Reversibility, T- and P-Dependence, …)

Task 3: Mesoporous Polymer Nanostructures (Synthesis, Hydrogen Uptake, …)

Task 4: Improved Fuel Cell Membrane

Task 5: Design and Characterization of Improved Fuel Cell Catalytic Materials
Hydrogen storage in/on nanomaterials

Titanium-decorated Carbon Nanotubes as a Potential High-capacity Hydrogen Storage Medium

a C\textsubscript{8}TiH\textsubscript{8} (5.3 wt%)  
b C\textsubscript{4}TiH\textsubscript{8} (7.7 wt%)

FIG. 3 (color online). Two high-density hydrogen coverage on a Ti-coated (8, 0) nanotube.
Single-Walled Carbon NanoTubes (SWNT)

- nanotubes come in bundles
- Samples have a size distribution
- Samples contain impurities

A local experiment on one individual nanotube would be ideal!

Which is the best nanotube for hydrogen storage?
How does hydrogen adsorption/desorption work?
How can we improve it?
Transition-metal decoration and hydrogen storage (Changfeng Chen, Physics, Task 1)

The binding energy of $H_2$ on Sc is slightly lower than that on Ti.

<table>
<thead>
<tr>
<th>Ti</th>
<th>$1H_2$</th>
<th>$2H_2$</th>
<th>$3H_2$</th>
<th>$4H_2$</th>
<th>$5H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (eV/H$_2$)</td>
<td>0.60</td>
<td>0.36</td>
<td>0.39</td>
<td>0.09</td>
<td>0.02</td>
</tr>
</tbody>
</table>

• Up to 4 $H_2$ are adsorbed on each Ti atom with the binding energy ranging from 0.1 eV to 0.4 eV per $H_2$. (7.8wt% for double side coverage)
A novel class of 3D nanoframeworks based on CNTs
(Balakrishnan Naduvalath, Chemistry, Eunja Kim, Physics, Task 1)

- Car-Parrinello molecular dynamics simulations indicate that the proposed frameworks are thermodynamically stable up to 20 ps at 300 K and 2 ps at 600K
- Preliminary results indicate that Li-decorated 3D nano-frameworks are promising for hydrogen storage
Electronic structure of Titanium clusters (B. Naduvalath, Task 1)

- $\text{Ti}_n$ clusters evolve on **Pentagonal** growth pattern
- Second energy difference indicates $\text{Ti}_7$ and $\text{Ti}_{13}$ clusters are highly stable, which agrees well with the experimental results

**Second Energy Difference**

$$\Delta_2 E = E(n+1) + E(n-1) - 2E(n)$$
Ti$_{13}$ cluster and H$_2$ saturation (B. Naduvalath, Task 1)

- Hydrogen multi-center bonds in Ti$_{13}$H$_m$
- $\mu_3$ for $m \leq 20$ and $\mu_2$ in Ti$_{13}$H$_{30}$
- Cage expansion due to saturation from $m = 20 – 30$ by 6%
Surface and interface spectroscopy/microscopy of nanomaterials for hydrogen storage (Clemens Heske, Chemistry, Task 1)

Experiment matrix for Hydrogen storage on (metaldecorated) carbon nanomaterials:

– Carbon (nano)materials: C\textsubscript{60}, SWNT, HOPG
– Metal (co-)adsorbates: Ti, Li
– Hydrogenation: molecular, atomic

• How does Hydrogen interact with carbon-based nanomaterials?
• Why is there a “gap” between theory and experiment?
Soft X-ray spectroscopies

- Photoelectron-Spectroscopy (PES)
- Auger-Electron-Spectroscopy (AES)
- X-Ray Emission Spectroscopy (XES)
- X-ray Absorption Spectroscopy (XAS)
Scanning Tunneling Microscopy (STM) / Spectroscopy (STS)

**Microscopy**

- Tunneling tip can be scanned over the sample by piezos
- Tunneling current is measured at a tunneling voltage $V$ and kept constant by a feedback controlling the $z$-direction → “topography of electron density”

**Spectroscopy**

- Tunneling voltage $V$ is varied at one spot with constant tip-sample distance → density of states around $E_F$

$$I(V) = \int_{0}^{eV} \rho_s(E) \cdot \rho_t(E - eV) \cdot T(E, eV, d)dE$$

$$\rho_s(eV) \approx c \cdot \frac{dI(V)}{dV}$$

HOPG 2x2 nm$^2$
STM on SWCNT – 2

- Electro-deposited (6 min, upside down) on HOPG, SWCNT (not cut)

Electro deposition worked

- Low coverage with long SWCNT
  - “Small” bundles (e.g. two bundled tubes) and individual tubes are observed
  - Atomic resolution can be achieved
Scanning Tunneling Microscopy/Spectroscopy of SWNT with/without Ti decoration (Task 1)

STM image of SWNT on Au with atomic resolution

I-V curve and STS of SWNT on Au

Ti deposited on top of SWNT/Au
Atomic Hydrogen Source (AHS)


Atomic hydrogen is produced by high temperature thermal cracking of molecular hydrogen via a W capillary tube, submitted to HV and electron bombardment

Atomic Hydrogen Source components:

• Gas Reservoir
• Tungsten Capillary Tube
  – 50-mm long, 1.6-mm O.D, 0.6-mm I.D.
  – Acceleration Voltage of ~+3 kV
• Tungsten Filament
  – 1.7 A, 7.0 V, 12 W
1. No shift in C 1s for molecular hydrogen adsorption (at RT)

2. C 1s shifts to higher binding energy for atomic hydrogen (along with capillary temperature), indicating H adsorption
XPS: Hydrogenation of SWNT (Task 1)

Normalized intensity (a.u.)

Sample

Normalized intensity (a.u.)

2 min. 2050K

W Capillary tube Temperature (K)

(0 stands for original sample)

A_{II}/A_{I}

A_{I}

A_{II}

Exp. curve
Fitted curve
Peak I
Peak II
Peak III

Normalized intensity (a.u.)

Binding Energy (eV)

Exp. curve
Fitted curve
Peak I
Peak II
Peak III

Binding Energy (eV)

A_{II}/A_{I}

0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00

0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200

0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00

W Capillary tube Temperature (K)
Gibbs free energy and temperature-pressure phase diagram of lithium alanates (Changfeng Chen, Task 2)

Apply first-principles electronic structure and lattice dynamics calculations within and beyond the harmonic phonon approximation to examine the thermodynamic phase stability of lithium alanates and predict their reaction pathways and reversibility

**Results:**
- Obtained a comprehensive set of thermodynamic functions over a wide temperature range for LiAlH₄, Li₃AlH₆ and LiH.
- Evaluated decomposition reactions to determine reversibility and suitability for practical use in mobile applications.
- Established the thermodynamic (temperature-pressure) phase diagram for lithium alanates and identified key operating physical parameters for hydrogen storage and reversible release-recharge process.
Polyaniline (PANI)/Pd Composites for Hydrogen Storage (David Hatchett, Task 3)

Pd(ii) reduction in PANI

Pd morphology is a function of the number of voltammetric cycles

Pd aggregation also possible with potentiometric growth
PANI/Pd Composites (Task 3)

Pd(iv) Reduction in PANI

Pd thickness is a function of the number of voltammetric cycles
H Sorption Apparatus (Task 3)
Hydrogen Sorption in Chemical Composites (Task 3)

Material A

Sorption is obtained using a normal GC with a hydrogen generator

- The first peak remains unchanged relative to the second because it represents the void volume of hydrogen in the tube rather than sorbed hydrogen
- The second peak represents sorbed hydrogen
- A temperature ramp is used to observed desorption
Hydrogen Sorption Results and Conclusions (Task 3)

- Five composite materials have been produced that show promise for Hydrogen sorption.
- Preliminary measurements have been made to verify the sorption properties.
- Variations in the chemical composites have been eliminated by treatment with NaBH₄ thus reducing any unreduced species.
- This material shows the highest sorption suggesting that treatment of the other chemically prepared composites may increase sorption properties.
Summary

FCAST is a joint experimental and theoretical project to enhance the understanding of hydrogen fuel cells and storage materials

- Joint experimental and theoretical work performed on electronic structure of carbon nanoclusters
- Stable structures of graphitic-BC$_2$N as potential hydrogen storage media identified
- The electronic structure of Ti decorated SWCNTs explored using X-ray and electron spectroscopy. Significant oxidation of Ti leading to TiO$_2$ formation is observed
- Systematically explored hydrogen uptake of transition metal-bonded organometallic systems (Sc, Ti, V) using DFT methods
- Proposed new class of carbon nanoframeworks (thin SWCNTs linked by phenyl spacers) as potential hydrogen storage media
- Investigated electronic structures and bondings in hydrogen saturated Ti and Ti-Al clusters and identified novel bonding motifs which may be harnessed to design novel hydrogen storage systems
- Synthesized bulk quantities of mesoporous PANI/Pd composites for hydrogen storage

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