Designing Microporous Carbons for Hydrogen Storage Systems
carried out in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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Air Products and Chemicals, Inc.
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This presentation does not contain any proprietary or confidential information
Air Products and Chemicals – Participation in DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

- Conceptual System Design
  - System engineering guidance, heat integration

- Computational Studies of Hydrogen Adsorption on Carbon-based Materials and New Computational Methods Development
  - Develop accurate and efficient computational methodologies, to be shared with other partners
  - Mechanistic studies of hydrogen adsorption

- Advanced Measurements of Hydrogen Adsorption
  - Exploration of a novel low-cost, high-throughput technique
  - Measurement assistance for other center partners and confirmation of important adsorption results from other partners

- Activation and Adsorption Characterization of Carbon-based Materials
  - Novel approaches to carbon-based adsorbents in collaboration with other partners
Carbon-based Hydrogen Storage Center: Work Plan and Timeline

Task 4: Activation and Adsorption Characterization of Carbon-based Materials
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

Task 3: Advanced Measurements of Hydrogen Adsorption
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

Task 2: Computational Studies of Hydrogen Adsorption on Carbon-based Materials and New Computational Methods Development
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

Task 1: Conceptual System Design
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

Focused Materials Development Manufacturability
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

System Measurements Capacity, kinetics, heat, safety Impurity tolerance
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

1 kg H₂ System Construction
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010

Material/Approach Center
- Go/No-Go
- Go/No-Go

Phase One
- FY2005
- FY2006
- FY2007

Phase Two
- FY2008
- FY2009
- FY2010

Major task milestone
- FY2005
- FY2006
- FY2007
- FY2008
- FY2009
- FY2010
Conceptual System Design: System Engineering Model of Adsorption

- Langmuir isotherm model assumes a $\Delta H$ of -25 kJ/mol and $\Delta S$ of -105 J/mol·K
- The “tank” can deliver 7.56 wt. % $H_2$ under these modeling conditions

Gravimetric hydrogen capacity is linked to the heat ($\Delta H$) and the entropy ($\Delta S$) of $H_2$ sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture. The sorbent ($S$) and $H_2$ equilibrium is expressed as:

$$S(s) + H_2(g) \xrightarrow{K} S \bullet H_2(s) \quad \text{where} \quad K = \frac{[S\bullet H_2]}{[S]P_{H_2}} \quad \text{(atm}^{-1})$$
New Computational Methods: Results and Future Development

- **Results:** Curvature dependent force field – tested and available to CoE partners
  
  The calculated optimal distribution of H₂ and the average adsorption energy (kcal/mol) per H₂
  
  The uncertainty of the averaged adsorption energy is approximately ±0.5 kcal/mol

<table>
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<th>nanotube (n,m)</th>
<th>SWNT diameter (Å)</th>
<th>0.4 wt. % H₂ loading</th>
<th>3.0 wt. % H₂ loading</th>
<th>6.5 wt. % H₂ loading</th>
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<td>$\Delta E_{ad}$ (kcal/mole)</td>
<td>endo/exo ratio</td>
<td>$\Delta E_{ad}$ (kcal/mole)</td>
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- **Results:** Constant NPT molecular dynamics: implemented in the AIREBO simulation package

- **Future methodology development:**
  
  - Reliable & transferable force field development
  
  - Grand Canonical Monte Carlo (GCMC) simulations: under development in AIREBO
  
  - Density functional theory with correct dispersion forces: to be implemented in SIESTA
New Computational Methods Development: Curvature-Dependent Force Field

- **Bonding Interaction**: Brenner’s bond order potential for C-C, H-H
- **Nonbonding Interactions**: must be curvature dependent

\[
\sigma (r) = f (r) \sigma_{sp}^2 + [1 - f (r)] \sigma_{sp}^3
\]

\[
\epsilon_{exo} (r) = f (r) \epsilon_{sp}^2 + [1 - f (r)] \epsilon_{sp}^{head-on}
\]

\[
\epsilon_{endo} (r) = f (r) \epsilon_{sp}^2 - [1 - f (r)] \epsilon_{sp}^{side-on}
\]

\[
f (r) = \left(1 - \frac{r_0}{r}\right)^\lambda \quad 0 < f (r) < 1
\]


Computational Studies of Hydrogen Adsorption on Carbon-based Materials

- **H₂ adsorption in carbon nanomaterials** (nanotubes, nanohorns, nanofibers, etc.)
  - Objectives: study storage capacity at given pressure and temperature and identify material properties key to adsorption
  - Methods: NPT-MD, GCMC
  - Potential collaborators: Rice University, NREL

- **H spillover onto carbon nanomaterials** (nanofibers, nanotubes, etc.)
  - Objectives: evaluate energetics for H spillover, identify chemisorption pattern, kinetics
  - Methods: Monte Carlo, DFT, MD
  - Potential collaborators: Rice University U. of Michigan, NREL

Electrostatic potential mapped to the electron density of a deformed (5,5) singlewalled carbon nanotube
Advanced Measurements of Hydrogen Adsorption: Differential Pressure Adsorption

- Differential pressure measurement more accurate than standard (absolute pressure) volumetric adsorption
- Equally accurate at low and high pressures (up to 120 bar)
- High temperature helium pycnometry will enable accurate hydrogen isotherms (unit under construction)
Advanced Measurements of Hydrogen Adsorption: Exploration of a Novel Low-cost, High-throughput Sorption Measurement Technique

- Direct method that measures the total amount of hydrogen (sorbed + gaseous) stored in a pressurized vessel containing a sorbent
- Measurements can be performed at ambient to high temperatures and high hydrogen pressures
- Inexpensive technique (requires an accurate analytical balance)
- Potential for high throughput screening
Activation and Adsorption Characterization of Carbon-based Materials: Potential Collaborations

- Hydrogen adsorption on small diameter singlewalled carbon nanotubes
  - Potential collaborations: Rice University, Duke University, NREL

- Boron and nitrogen incorporation into carbon nanostructures
  - Potential collaboration: Penn State University

- Doping of carbon nanotubes
  - Enhancing heat of adsorption of hydrogen as indicated by predictive computational modeling
  - Potential collaboration: California Institute of Technology

Laser light scattering profile of SWNT samples before (dotted line) and after (solid line) a non-destructive cutting procedure

Transmission Electron Microscopy
Overview

Timeline

- Project start date FY05
- Project end date FY09
- New start

Barriers

- Technical Barriers-Hydrogen Storage
  A. Cost
  B. Weight and Volume
  C. Efficiency
  E. Refueling time
  M. Hydrogen Capacity and Reversibility
  N. Lack of Understanding
  O. Test Protocols
  Q. Thermal Management

Budget

- Total project $3,539,750
  - DOE share $2,842,540 (80%)
- FY05 funding $300,000

Partners

- Current interactions: NREL
- Anticipated collaborations: Rice University, Duke University, University of Michigan