Carbon Aerogels for Hydrogen Storage

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Project ID: ST-24
Project Overview

Timeline
• Project start: FY05
• Project end date: FY09
• Percent complete: 75%

Budget
• Total project funding (proposed): $1050K
• Funding received in FY07: $390 K
• Funding for FY08: $470 K
  • 0.5 FTE + 1.0 Post-Doc

Technical Barriers Addressed by Project
A. System Weight and Volume
C. Efficiency
P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners
• CalTech (Prof. Ahn)
  • H₂ adsorption measurements
• NIST (C. Brown)
  • Characterization by Neutron Scattering Experiments
• UNC-Chapel Hill (Prof. Wu)
  • Advanced NMR analysis
• HRL Laboratories (J. Vajo, MHCoE)
  • Scaffolds for Metal Hydrides
Project Objectives

- Our objective is the design of novel carbon aerogel (CA) materials that meet the DOE system targets (6 wt%, 45 g/L) for on-board vehicle H₂ storage

- Current focus in two areas:
  - Engineering of CA-based spillover materials:
    - Optimize structure for enhanced H₂ uptake and improved kinetics
    - Storage at reasonable operating temperatures
  - Design of new CA materials as porous scaffolds for metal hydride materials:
    - Potential to improve kinetic and thermodynamic performance of metal hydrides

FY07
- Engineering undoped CAs
- Evaluation of H₂ Sorption
- Screening of CA Scaffolds

FY08
- Dopant Incorporation
- Spillover/Kinetics Study
- CA Scaffold Engineering

FY09
- Mechanistic Studies
- Reversibility/Lifetime Studies for CA Sorbent and Scaffolds
Project Approach

- Our approach is to utilize the flexibility of CA synthesis for the design of new carbon-based spillover materials and metal hydride scaffolds.
- CA synthesis allows for control over bulk properties (surface area, pore size, pore volume, density) and for the homogeneous incorporation of dopants (metal catalysts) into the CA matrix.
- This approach allows us to control the size and dispersion of H₂ dissociation catalysts as well as the surface chemistry and microstructure of the support in spillover systems.
- We can also use this flexibility to design novel nanocomposites that possess the requisite structural properties (large pore volumes, small pore sizes) for metal hydride scaffolding.
Previous Accomplishments

• Previous work focused on engineering the CA structure to maximize number of sites available for interaction with hydrogen

• The CA structure (surface area, pore size) was modified through a combination of sol-gel chemistry and thermal activation

• Microporous CAs with surface areas in excess of 3000 m²/g were prepared

• Hydrogen uptake in the activated CAs was reversible

• Surface excess H₂ adsorbed at 77K for high surface area CAs varies linearly with SA up to ~2500 m²/g (weaker dependence at higher SAs)

• CAs exhibited H₂ density of 5.3 wt% and 29.2 g H₂/L at 77K

Technical Accomplishments: Design of CA-based spillover materials

- Improved performance in spillover materials (uptake and kinetics) requires synthetic methods that provide control over:
  - Loading, size and dispersion of the dissociation catalyst
  - Interface between the catalyst particle and the support surface
  - Surface chemistry and microstructure of the support material

- These structural features can be readily modified through CA synthesis (i.e. doping method, aerogel structure) to optimize spillover process for H₂ storage

- We have investigated the influence of different metal-doping methods on the performance of CA-based spillover materials:
  1. Functionalized CA precursors¹
  2. Impregnation and reduction of metal salts²
  3. Vapor deposition techniques, such as atomic layer deposition (ALD)³


Technical Accomplishments: H₂ Sorption in Metal-doped CAs

- Ni- and Pt-doped CAs (8-10 wt%) prepared by the CA precursor method did not show spillover behavior at room temperature
  - Likely due to inaccessibility of metal particles in carbon support
- These materials do exhibit unusual H₂ sorption at 77 K:
  - Higher H₂ gravimetric density than expected according to the Chahine correlation (1 wt% H₂ per 500 m²/g SA)
  - Enhanced sorption enthalpies relative to undoped CAs (>7 kJ/mol)

![Metal-doped CA](image)

**Pt-doped CA at 77 K**
- BET SA of Pt-CA ~ 640 m²/g
- Surface excess H₂ ~ 1.8 wt%
  - 1.4 wt% per 500 m²/g

![Graph showing H₂ adsorption vs. pressure](image)
Technical Accomplishments: 
H₂ Sorption in Metal-doped CAs

• Metal dopants were incorporated into the high surface area CAs through impregnation using R. Yang’s procedure¹:
  • Activated CAs (1400 and 2400 m²/g) were treated with H₂PtCl₆ that are subsequently reduced with H₂ to form metal nanoparticles
  • Both Pt-doped ACAs exhibit spillover behavior at RT:
    • Isotherm for 2400 m²/g Pt-CA extrapolates to 1.2 wt% H₂ at 100 bar
    • H₂ isotherms shows slight dependence on surface area
    • Observation indicates non-optimal dispersion of catalyst particles

¹Yanq et al., J. Phys. Chem. C 2007, 111, 11086
Technical Accomplishments: Atomic Layer Deposition on CAs

- Advances in RT H₂ uptake by spillover can be achieved through improved design of sorbent material:
  - Diffusion distances of H appear to be short (< 1 nm) in C-based materials
  - Optimized dispersion of dissociation sites on support surface is therefore critical to increased H₂ uptake
- We are investigating atomic layer deposition (ALD) as a method to improve dispersion of Pt in CA structure
  - ALD¹: Self-limiting form of CVD that provides atomic level control of material deposition
  - Process can be used to deposit material into high aspect ratio structures, such as the porosity of aerogels²

Technical Accomplishments: Pt ALD on CAs

- New spillover materials were prepared through ALD of Pt on high surface area CAs

HR-TEM of Pt-doped ACA (2400 m²/g)
Prepared by atomic layer deposition
[CpPtMe₃/O₂], 2 cycles
ALD performed by the Bent Group at Stanford

- Overall H₂ uptake is lower due to incomplete Pt deposition
- Important aspect of material performance is improved kinetics:
  - Shorter times required for system to reach equilibrium (30 min vs 2-4 hrs)
• We are fabricating CAs as scaffolds for light metal hydrides (LMH), such as MgH$_2$, LiBH$_4$ and NaAlH$_4$
  
  • Work with HRL Laboratories (Metal Hydride CoE)

• Nanoporous scaffolds can improve kinetics of metal hydrides by limiting particle size and reducing diffusion distances$^{1,2}$

• Structural requirements for scaffolding materials:
  
  • Large pore volumes (minimize capacity penalty)
  • Small pore sizes (limit particle sizes)
  • Good thermal conductivity
  • Compatible surface chemistry

• Our focus has been on the design of novel CA nanocomposites that possess the requisite properties for MH scaffolding

• CA scaffolds are delivered to HRL for MH infiltration (LiBH$_4$, Mg) and evaluation of MH-scaffold performance


Yu et al, Appl. Phys. Lett. 2007, 90, 03410;
Technical Accomplishments: New CAs Scaffolds

- New CAs with small pore sizes and larger pore volumes have been prepared using a templating approach:
  - Sacrificial template incorporated into aerogel matrix during the sol-gel reaction and removed during carbonization
  - New material combines the large pore volumes of the our original CAs with the small pore size of HRL xerogels

New CA Scaffold
APD ~ 15 nm
PV = 2.6 cm$^3$/g

HRL Carbon Xerogel
APD ~ 13 nm
PV = 1.1 cm$^3$/g

Previous LLNL CAs
APD ~ 9.5 nm
PV = 1.1 cm$^3$/g

CA with small pore sizes (< 5 nm) delivered to NIST (Jack Rush) for LiBH$_4$ study

- CA with small pore sizes (< 5 nm) delivered to NIST (Jack Rush) for LiBH$_4$ study
We have also incorporated carbon nanotubes (CNTs) into the CA framework with the goal of enhancing thermal conductivity.

- CNTs could also be used as “plumbing” for $\text{H}_2$ transport within scaffold.

CA-CNT composites have been prepared with large pore volumes (~4 cc/g), but larger pore sizes (> 20 nm).

Composites also exhibit enhanced thermal conductivities:

- **CA-CNT (6 wt%):** 0.072 W m$^{-1}$ K$^{-1}$ vs **CA:** 0.036 W m$^{-1}$ K$^{-1}$

Future Work

• Evaluation of RT H$_2$ uptake in metal-doped CAs:
  • Utilize ALD for improved dispersion of catalysts (FY08)
  • Investigate alternative H$_2$ dissociation catalysts (i.e. Ni) (FY08)
  • Control over structure of CA support may provide some mechanistic insights into spillover diffusion processes (FY08-09)
  • Determine kinetics of H$_2$ uptake/release in spillover systems (FY09)
  • Develop methods to “monitor” spillover process (advanced NMR or x-ray absorption/emission techniques?) (FY09)

• Optimization of CA scaffolds for metal hydrides:
  • Engineering of CA structure (porosity, composites) (FY08-09)
  • Modify CA surface chemistry to improve MH wetting behavior (FY09)
  • Incorporation of catalysts/destabilizing agents (FY09)
  • Evaluate reversibility and lifetime in these materials over multiple charge/discharge cycles
Project Summary

Relevance: Design of new CA materials for hydrogen storage

Approach: Incorporation of dopants into high surface area CA to maximize $H_2$ uptake and modify binding energies

Technical Accomplishments:

- Synthesized new high surface area metal-doped CA that exhibited RT uptake of hydrogen (1.2 wt% at 100 bar)
- Fabricated new spillover materials with enhanced $H_2$ uptake kinetics using atomic layer deposition
- Prepared new CA nanocomposites as scaffolds for metal hydride systems

Center Collaborations:

- Prof. Channing Ahn (CalTech): $H_2$ sorption measurements
- Craig Brown (NIST): Characterization of activated CA structure by NS techniques
- Prof. Yue Wu (UNC): Characterization of CA structure and $H_2$ uptake by advanced NMR techniques
- John Vajo (HRL, MHCoE): CA scaffolds for metal hydrides
## Summary for CA Materials

### DOE On-Board Hydrogen Storage System Targets

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010 System Target</th>
<th>FY07 CA Material Results</th>
<th>FY08 CA Material Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>kWh/kg (wt% H₂)</td>
<td>2.0 (6 wt% H₂)</td>
<td>5.3 wt% at 77 K and 30 bar(^1)</td>
<td>1.2 wt% at RT and 100 bar(^2)</td>
</tr>
<tr>
<td>Energy Density</td>
<td>kWh/L (g H₂/L)</td>
<td>1.5 (45 g H₂/L)</td>
<td>~29 g H₂/L</td>
<td>TBD</td>
</tr>
</tbody>
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\(^1\)Undoped CA with BET surface area ~3100 m²/g  
\(^2\)High surface area CA (~2400 m²/g) doped with Pt (6 wt%)