Carbon Aerogels for Hydrogen Storage

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This presentation contains no confidential or proprietary information

Project ID: ST077
Project Overview

Timeline
• Project start: FY05
• Project end date: FY10
• Percent complete: 100%

Budget
• Total project funding (proposed): $1050K
• Funding received in FY09: $470 K
• Funding for FY10: $302 K

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)
  • MOF processing
• 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 aerogel materials that meet the DOE system targets (6 wt%, 45 g/L) for on-board vehicle H₂ storage

• Efforts were focused in two areas:
  • Engineering of aerogel-based sorbent materials:
    • Optimize structure for enhanced H₂ uptake and improved kinetics
    • Storage at reasonable operating temperatures
  • Design of aerogel materials as porous scaffolds for light metal hydride systems:
    • Potential to improve kinetic and thermodynamic performance of metal hydrides

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<td>Spillover/Kinetics Study</td>
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<td>Screening of CA Scaffolds</td>
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<td>Reversibility/Lifetime Studies for Sorbent and Scaffolds</td>
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Project Approach-Part 1

• Our approach is to utilize the flexibility of aerogel synthesis for the design new sorbent materials

• Aerogel synthesis allows for control over bulk properties (surface area, pore size, pore volume, composition, density) and for the homogeneous incorporation of modifiers (metal catalysts, organometallic species) into the matrix

• With this approach, we can control:
  • Surface chemistry and microstructure of the sorbent
  • Dispersion of the modifier (i.e. Pt nanoparticles for spillover)

• We can also use this flexibility to explore other sorbent materials with unique compositions

• Process is scaleable for production of monoliths or powders
Project Approach-Part 2

• Improved reaction kinetics for reversible H₂ storage in complex metal hydrides can be achieved through use of nanoporous scaffolds
  • Limits particles sizes and reduces diffusion distances
• We are fabricating aerogels as scaffolds for light metal hydrides (LMH), such as MgH₂, LiBH₄ and NaAlH₄
  • Work with HRL Laboratories (Metal Hydride CoE)
• Structural requirements for practical application of MH scaffolds:
  • Large pore volumes (minimize capacity penalty)
  • Small pore sizes (limit particle sizes)
  • Good thermal conductivity
  • Compatible surface chemistry
• We are using the flexibility of aerogel synthesis to design novel nanocomposites that possess the requisite structural, chemical and transport properties for metal hydride scaffolding
Previous Accomplishments: 
Activated CA Sorbents

- Microporous CAs with surface areas in excess of 3000 m²/g were prepared that exhibited surface excess H₂ adsorption of up to 5.3 wt% and 29.2 g H₂/L at 77K.

- These high surface area materials were used as supports for the design of new spillover materials with the goal of increasing overall H₂ capacity and improving uptake kinetics at room temperature.

- Hydrogen dissociation catalysts (Ni, Pt) were incorporated into the aerogel supports by different methods to investigate the effects of catalyst dispersion and catalyst/support interface on H₂ uptake and kinetics.

- Spillover systems derived from CAs exhibited significant issues with reproducibility for H₂ uptake at RT.

HR-TEM of Pt-doped ACA (2400 m²/g) prepared by atomic layer deposition.
Technical Accomplishments: Controlling Pore Size in Activated CAs

- New activated CAs have been prepared that exhibit higher bulk densities and increased micropore content:
  - Focus on increasing volumetric capacities in our ACAs
  - Improved textural properties achieved through modified thermal activation process
  - Smaller average pore sizes observed for KOH-activated CAs

- Bulk densities of the high surface area ACAs is also improved

- Hybrid CO$_2$-KOH activation process may provide access to ACA with desired pore structure

- Current target is an ACA with surface area ~2700 m$^2$/g (> 5 wt% H$_2$) that exhibits high bulk density (> 0.5 g/cc) and narrow micropore size distribution (< 10 Å)

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1Similar approaches have recently been reported: Meisner et al, Nanotech. 2009, 20, 204023; Wen et al, Electrochem. Comm. 2009, 11, 715.
Technical Accomplishments: New Spillover Receptors

- We have prepared new carbon aerogel materials derived from sugars that may have potential as spillover receptors:
  - Materials derived from carbonization of sucrose or glucose aerogels\(^1\)
  - Carbonized sugar aerogels (cSA) are comprised entirely of “bridge” material used to enhance hydrogen uptake in other spillover systems\(^2\)

- This material should exhibit very different surface characteristics than those of traditional activated carbons, especially with regard to oxygen-containing species
- Potential to improved kinetics of spillover process
- Current focus for cSAs:
  - Increasing surface area either through aerogel synthesis or thermal activation process
  - Incorporation of hydrogen dissociation catalysts (i.e. Ru)

2 Yang et al., *JACS*, 2006, 128, 8136.
Previous Accomplishments: CA Scaffolds

- New CAs were prepared and tested as scaffolds with LiBH₄:
  - The 2nd generation materials combined the large pore volumes of the 1st generation CAs with the small pore size of HRL xerogels

1st Generation
HRL Carbon Xerogel
APD ~ 13 nm
PV = 1.1 cm³/g

LLNL CA
APD ~ 40 nm
PV = 2.7 cm³/g

2nd Gen Scaffolds
APD ~ 15 nm
PV = 2.6 cm³/g

APD ~ 9.5 nm
PV = 1.1 cm³/g

APD ~ 4 nm
PV = 0.5 cm³/g

- LiBH₄ composites prepared with these scaffolds exhibited decreases in dehydrogenation temperatures relative to bulk LiBH₄

- We also synthesized new carbon nanotube (CNT)-CA composites as next-generation scaffold materials:
  - Improved thermal transport in these scaffolds
  - CNTs appeared to influence hydrogen desorption process for LiBH₄
Technical Accomplishments: Carbon Nanotube-CA Composites

• We have developed a new method for growing CNTs directly in the pores of the CA scaffold:
  • CVD growth of multi-walled CNTs within metal-loaded CAs (M=Ni, Fe)
  • CNTs fill the open pore volume of the scaffold
  • Approach provides larger interfacial area between CNTs and metal hydride

SEM and TEM images of MWCNTs grown in the pores of an ACA (2400 m²/g)

Technical Accomplishments: Carbon Nanotube-CA Composites

- LiBH₄ composites prepared with these CA-CNT scaffolds exhibited lower dehydrogenation temperatures than either the bulk hydride or composites made with the smaller pore CA scaffolds

TGA data for LiBH₄ incorporated into different CA scaffolds

- Dehydrogenation temperature is lower than expected based on the large average pore size of the CA-CNT scaffold (>100 nm)

- Interaction of BH₄ with CNT surface may influence rate of H₂ exchange, similar to the effect reported for LiAlH₄/CNT systems

- Metal catalyst nanoparticles (Ni) may also play role in dehydrogenation process

Technical Accomplishments: Surface Modification of Scaffolds

- We have also developed methods\(^1\) for preparing monolithic scaffolds with surface coatings that are inert and can improve the wetting characteristics of the scaffold for magnesium metal:
  - Metal carbide surfaces (i.e TiC) have been shown to exhibit better wetting compatibility with Mg than pure carbon surfaces\(^2\)
  - CA scaffolds coated with a uniform layer of TiC have been prepared

- These materials are prepared by a simple two-step process:
  - The scaffold is first coated with a thin layer of TiO\(_2\) using either vapor- or solution-phase techniques
  - The TiO\(_2\)-CA is then treated at 1400°C under Ar, leading to carbothermal reduction of the TiO\(_2\)
  - This approach allows for coating of the surfaces of the scaffold without compromising pore volume

Collaborations

• Partners:
  • CalTech (Academic): H₂ uptake measurements in spillover materials as well as new sorbent systems
  • HRL Laboratories (Industry): Evaluation of aerogels as scaffolds for metal hydrides
  • NREL (Federal): (1) Performance evaluation of new spillover materials and (2) testing of functionalized aerogels as supports for organometallic species
  • NIST (Federal): (1) Supercritical processing of MOF sorbents and (2) evaluation of scaffolding effects on performance of metal hydride materials by Neutron Scattering experiments
  • UNC-Chapel Hill (Academic): Advanced NMR analysis of H₂ sorption in high surface area sorbents
Future Work

• Complete work on modified synthesis/activation process to increase volumetric capacities of ACA:
  • Hybrid activation to control evolution of micropores
  • Improved architecture to increase bulk density
• Evaluate performance of new sugar-based spillover receptor:
  • Test spillover behavior (uptake, kinetics, reversibility) in metal-doped cSAs
• Optimize CNT-CA scaffolds for metal hydrides:
  • Continued engineering of scaffold structure (porosity, CNT-loading)
  • Modify surface chemistry of the scaffolds to improve MH wetting behavior
  • Incorporation of catalysts/destabilizing agents into CA-CNT composites
Project Summary

Relevance: Design of new aerogel materials for hydrogen storage

Approach: Incorporation of modifiers into high surface area aerogels to maximize H₂ uptake and increase binding energies

Technical Accomplishments:

• Improved pore size distribution in activated CAs
• Fabricated new spillover receptors derived from sugars
• Prepared novel CA-CNT nanocomposites as scaffolds for metal hydride systems

Center Collaborations:

• Prof. Channing Ahn (CalTech): H₂ sorption measurements
• John Vajo (HRL, MHCoE): CA scaffolds for metal hydrides
• Craig Brown (NIST): (1) Supercritical processing of MOFs and (2) Characterization of CA structure by NS techniques
• Prof. Yue Wu (UNC): Characterization of CA structure and H₂ uptake by advanced NMR techniques
## Summary for CA Materials

### DOE On-Board Hydrogen Storage System Targets

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<th>Units</th>
<th>2010 System Target</th>
<th>CA Material Results</th>
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<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</td>
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<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>
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