2006 DOE Hydrogen Program Review

Metal-doped Carbon Aerogels for Hydrogen Storage

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Project Overview

Timeline

- Project start: Jan 2005
- Project end date: Oct 2007
- Percent complete: 50%

Budget

- Total project funding (proposed): $1050K
- Funding for FY05: $240K
- Funding for FY06: $265K

Technical Barriers Addressed by Project

B. Weight and Volume

C. Efficiency

M. Hydrogen Capacity and Reversibility

N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

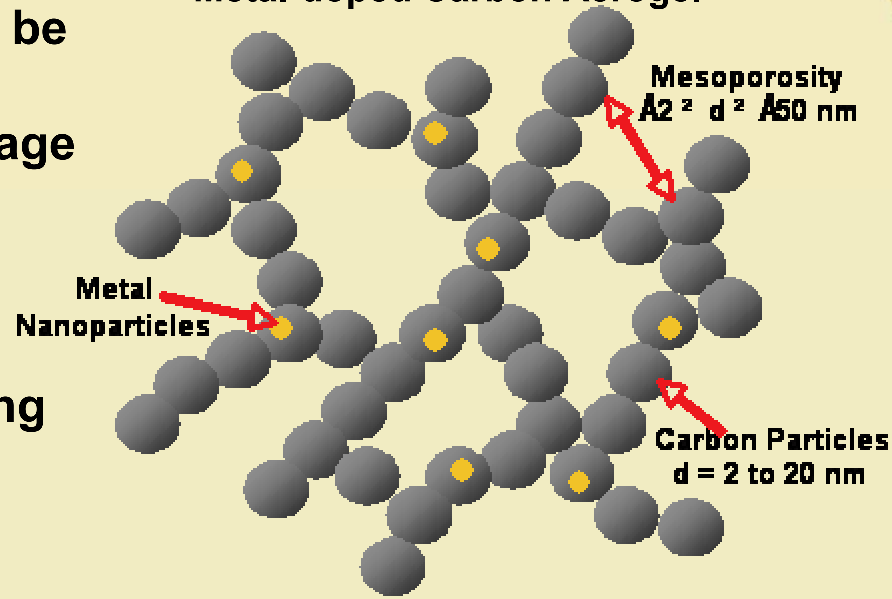
Partners

- CalTech (Prof. Ahn) for H_2 adsorption measurements
- UNC-Chapel Hill (Prof. Wu) for advanced NMR analysis

Project Objectives

- **Our objective is the design of new nanostructured carbon-based materials that meet the DOE 2010 targets for on-board vehicle hydrogen storage of 6 wt% H_2**
  - **Metal-doped carbon aerogels will be prepared, characterized and evaluated for their hydrogen storage properties**
  - **Mechanisms associated with hydrogen adsorption in these materials will be investigated using advanced nuclear magnetic resonance (NMR) techniques**

Metal-doped Carbon Aerogel



FY05	FY06	FY07
• Materials synthesis • Structural characterization	• Evaluate H_2 Adsorption • Refine Materials Design	• Mechanistic Studies • Reversibility/Lifetime Studies

Project Approach

- **Carbon aerogels are novel mesoporous materials that possess a number of desirable structural features for hydrogen storage:**
  - Low mass densities (0.02 to 1.2 g/cc)
  - Ultrafine cell/pore sizes
  - High surface areas (up to 1000 m^2/g)
  - Continuous porosities
- **In addition, carbon aerogels present a number of advantages for the design of hydrogen storage materials:**
  - Carbon aerogels can be readily prepared in large quantities as either monoliths or powders
  - Bulk properties of the carbon aerogel (i.e. density, surface area, pore size distribution, pore volume) are controlled through synthetic parameters
  - Surface area of carbon aerogels can be increased further by activation with CO_2 (up to ~2600 m^2/g)
  - Flexibility of sol-gel chemistry allows incorporation of dopants into the carbon matrix, such as boron or metal nanoparticles, to enhance H_2 uptake

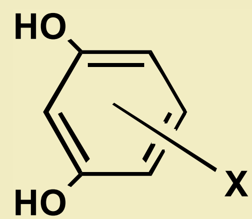
Project Approach

- Carbon aerogels are prepared using sol-gel chemistry:

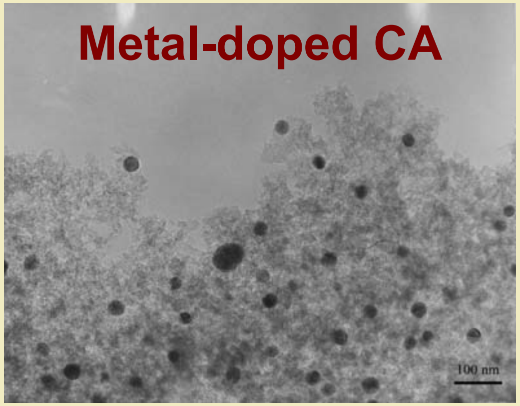
- Dopants, such as boron or metal catalysts, can be introduced into the carbon aerogel structure by two different methods:

  1. Functionalized sol-gel precursors:

     - Results in uniform distribution of dopant throughout aerogel framework
     - General method that can be extended to incorporate a variety of different moieties
     - Metals can be introduced through the use of resorcinol derivatives containing ion exchange sites
     - Metal ions are reduced and form nanoparticles during carbonization



Where X can be a metal-binding site or a boron-containing unit

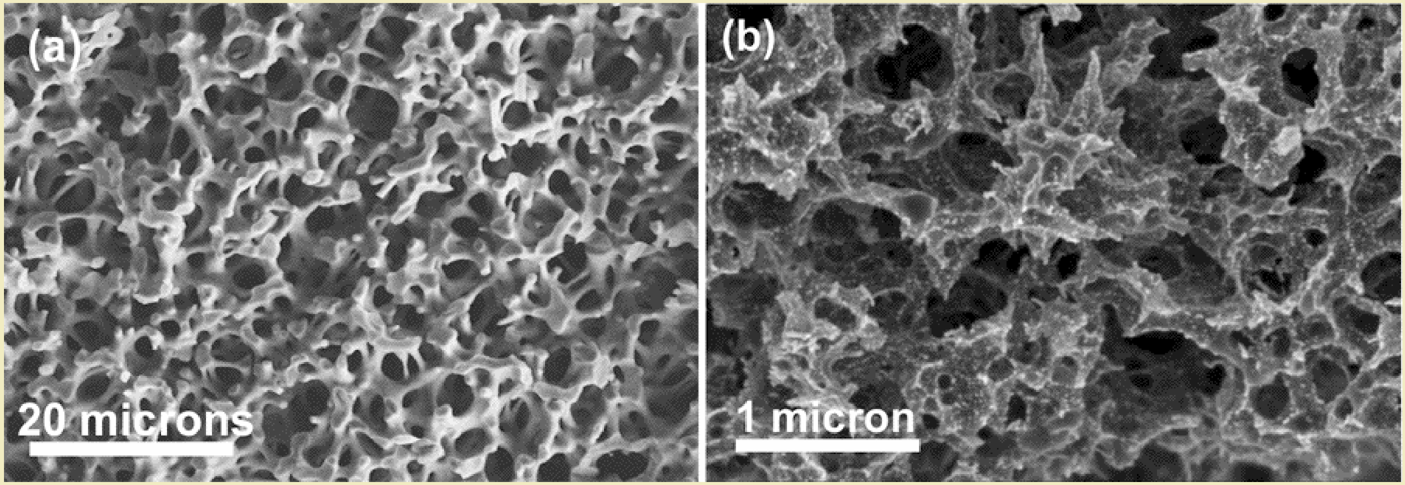


Project Approach

2. Metals (i.e. Ni or Pd) can also be introduced into the CA after CO_2 activation through atomic layer deposition (ALD):

- A process that provides atomic layer control of thin film growth through sequential, self-limiting surface reactions
- As a result, ALD can be used to deposit material inside high aspect ratio structures, such as the pores of an aerogel
- The surface chemistry of the substrate can be used to promote nanoparticle formation as opposed to conformal film growth

High surface area CA (a) before and (b) after Pt deposition



Pt nanoparticles are visible as bright spots on the carbon aerogel support

Technical Accomplishments

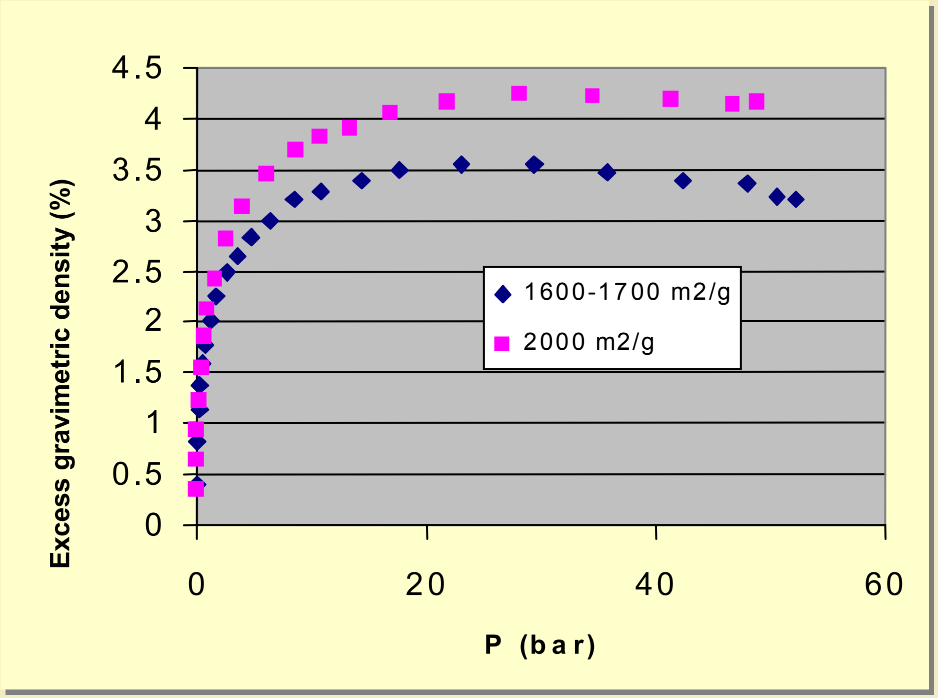
FY06 Accomplishments:

- **High surface area carbon aerogels have been prepared through CO_2 activation:**
  - Correlated the increase in surface area to activation time, aerogel density and morphology
  - Prepared materials with surface areas up to 2600 m^2/g
  - Structures of these materials have been characterized using SEM, TEM and XPS
  - Currently examining carbon structure and porosity in these materials using advanced solid state NMR techniques

- **H_2 adsorption in CAs was evaluated by Prof. Ahn at CalTech:**
  - Undoped and metal-doped CAs (M = Co, Ni) have been examined
  - H_2 gravimetric density tracks with CA surface area
  - CA with SA~2000 m^2/g exhibited gravimetric density ~ 4.2% at 77K
  - Metal dopants appear to alter sorption enthalpy in these materials

Technical Accomplishments

- H_2 gravimetric density in activated carbon aerogels with different surface areas were evaluated at CalTech
- H_2 adsorption isotherms for these materials were measured up to 40 bar at 77 K to obtain saturation values
- Hydrogen uptake was shown to be completely reversible

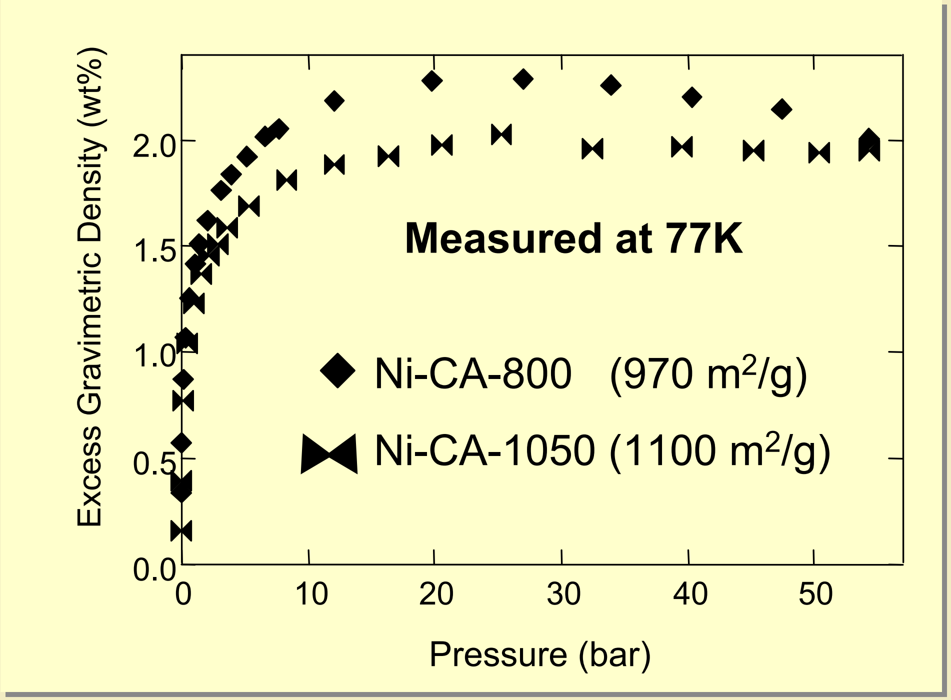


- CA with SA~2000 m²/g exhibited gravimetric density ~ 4.2% at 77K
- Assuming a *monolithic* density of ~ 0.55 g/cc, the volumetric capacity for this material would be ~ 23 g H_2/L

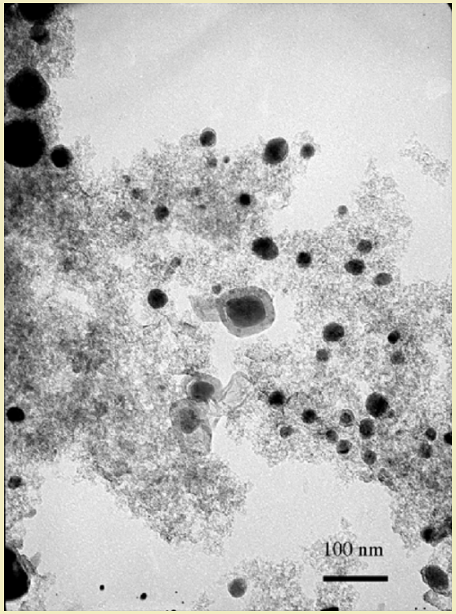
We are currently modifying the surface area and density of these materials to optimize the specific energy and energy density

Technical Accomplishments

- **Incorporation of metal nanoparticles into the CA framework appears to alter sorption enthalpy in the carbon aerogels:**
  - **Higher H_2 gravimetric density observed in the lower surface area Ni-doped CA material**
  - **Ni particles in Ni-CA-1050 are encapsulated in graphitic layers and are therefore inaccessible**



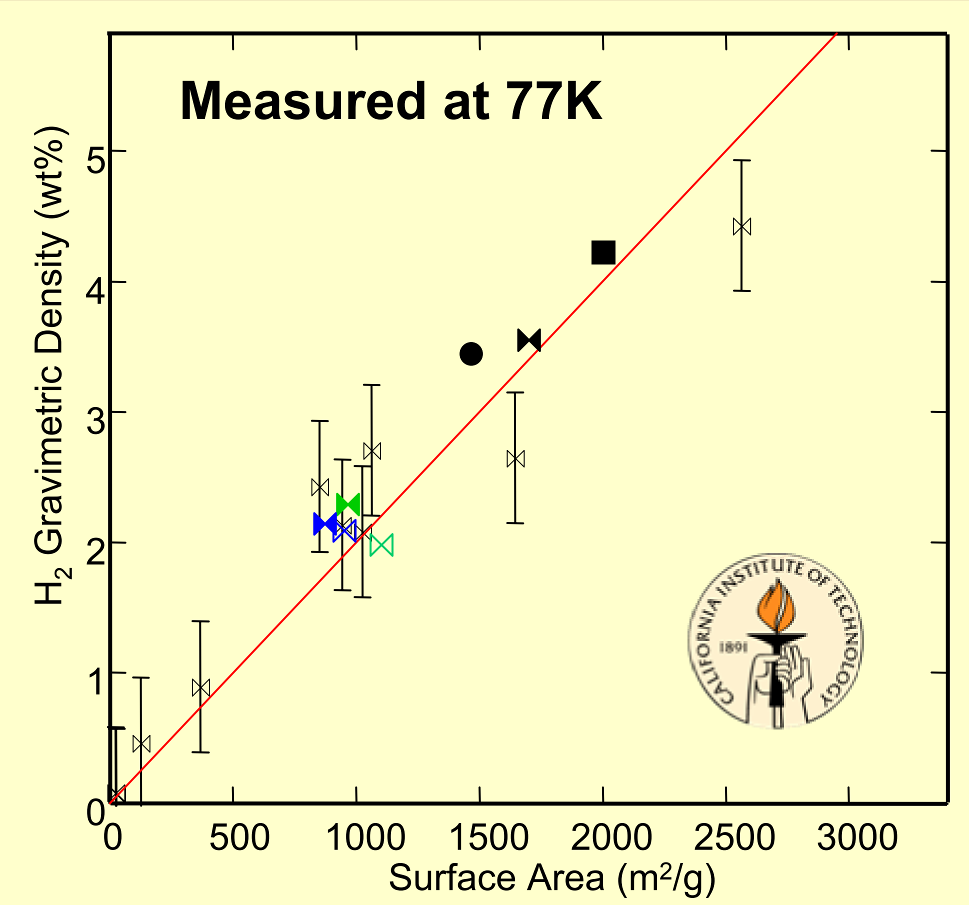
Ni-doped CA



Our next goal is the incorporation of metal dopants into the high surface area CAs (SA~2600 m^2/g)

Technical Accomplishments

- **Hydrogen adsorption in our carbon aerogel materials follows the "Chahine rule" of 1 wt% H_2 per 500 m^2/g of surface area (red line in graph)**



LLNL Materials

Undoped CAs

- ■ CA-2HA-b
- ⧓ CA-2HA-a
- ● CA-4HA

M-doped CAs

- Ni-CA-800
- Ni-CA-1050
- Co-CA-800
- Co-CA-1050
- ⋈ Panella data (*Carbon*, 2005)

Future Work

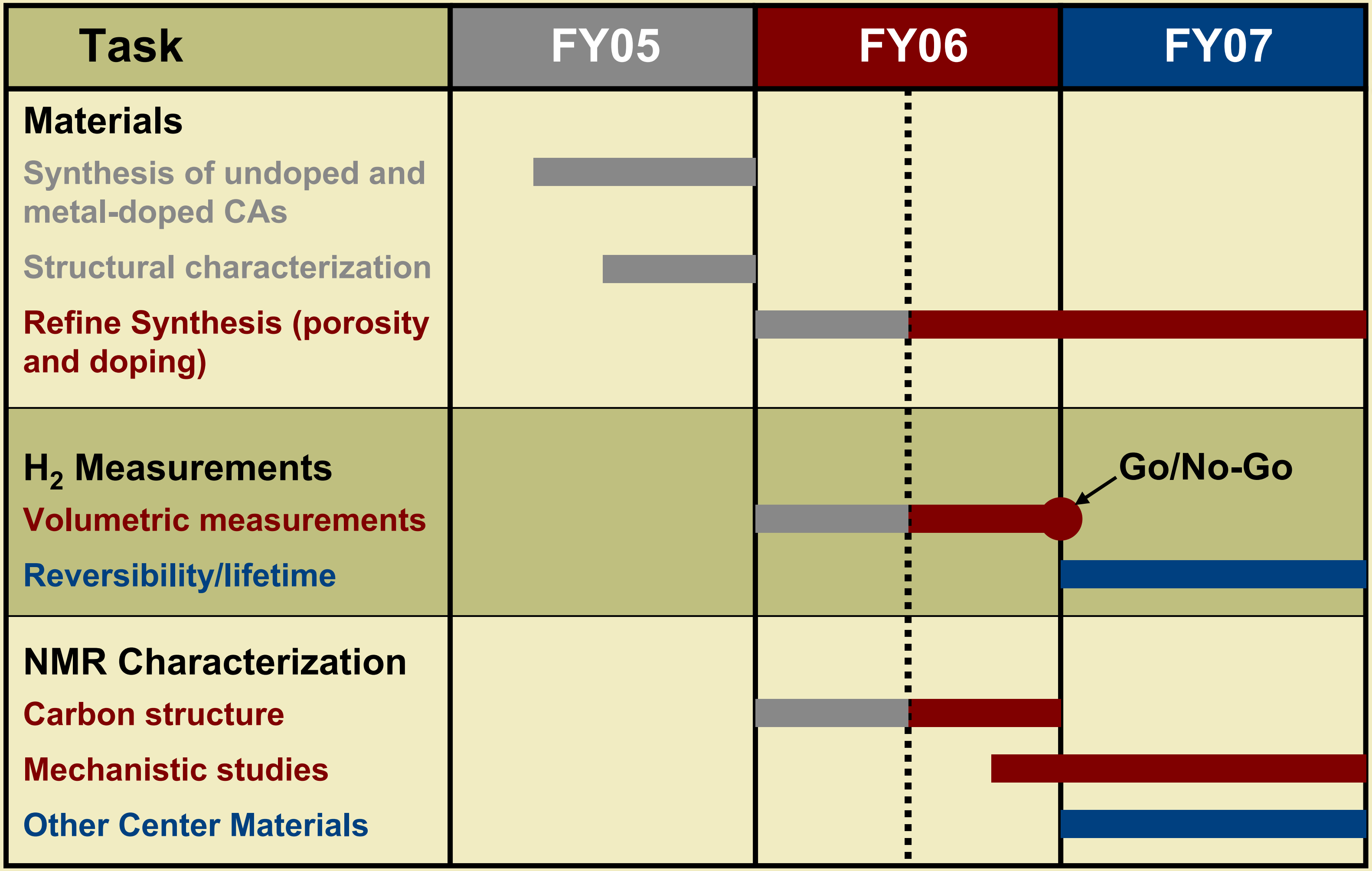
Continuing FY06 Efforts:

- **Utilize sol-gel chemistry to *tune* the bulk properties of CAs for H_2 adsorption**
  - **Increase microporosity while maintaining high surface areas and large pore volumes**
  - **Modify CA density to increase energy density in these materials**
- **Incorporate dopants into high surface area CAs**
  - **Metal nanoparticles, such as Ni or Pd, can be incorporated before (ion exchange) or after activation (atomic layer deposition)**
  - **Boron can be incorporated into carbon aerogel network through B-functionalized sol-gel precursors**

FY07 Efforts:

- **Initiate mechanistic studies of hydrogen uptake using advanced NMR techniques**
  - **Para-Induced Hydrogen Polarization (PIHP) NMR will be used to examine interactions between molecular hydrogen and carbon aerogel network**

Future Work


Task
FY05
FY06
FY07
Materials
Synthesis of undoped and metal-doped CAs
Structural characterization
Refine Synthesis (porosity and doping)
H_2 Measurements
Volumetric measurements
Reversibility/lifetime
Go/No-Go
NMR Characterization
Carbon structure
Mechanistic studies
Other Center Materials

Project Summary

Relevance: Design of new carbon-based materials for hydrogen storage

Approach: Incorporation of dopants into high surface area carbon aerogels to optimize H_2 uptake

Technical Accomplishments:

- Prepared and characterized carbon aerogels with surface areas as high as 2600 m^2/g
- CA with SA~2000 m^2/g exhibited gravimetric H_2 density of 4.2 wt% at 77K
- Metal nanoparticles appear to alter sorption enthalpies in these materials

Center Collaborations:

- Prof. Channing Ahn (CalTech) for H_2 uptake measurements
- Prof. Yue Wu (UNC-Chapel Hill) for NMR measurements

Current Work:

- CO_2 activation of metal-doped CA materials
- Incorporation of boron into carbon aerogel network
- Mechanistic studies using advanced NMR techniques

Summary Table

On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 System Target	FY06 Results[a]
Specific Energy	kWh/kg (wt% H_2)	2.0 (6 wt% H_2)	4.2 wt%[b]
Energy Density	kWh/L (g H_2/L)	1.5 (45 g H_2/L)	~23 g H_2/L[c]

[a]Data for material only, not system value
[b]Data for an undoped CA (SA~2000 m^2/g) collected at 77 K and 30 bar
[c]Calculated for a CA with *monolithic* density ~0.55 g/cm^3

Publications and Presentations

R. Fu, T. F. Baumann, S. Cronin, G. Dresselhaus,M. S. Dresselhaus and J. H. Satcher “Formation of Graphitic Structures in Cobalt- and Nickel-Doped Carbon Aerogels” *Langmuir*, **2005**, *21*, 2647.

I. L. Moudrakovski, C. I. Ratcliffe, J. A. Ripmeester, L. Q. Wang, G. J. Exarhos, T. F. Baumann and J. H. Satcher “Nuclear Magnetic Resonance Studies of Resorcinol-Formaldehyde Aerogels” *J. Phys. Chem. B* **2005**, *109*, 11215.

H. Kabbour, A. Saulnier, T. F. Baumann, J. H. Satcher and C. C. Ahn “Surface Area Dependence of Hydrogen Gravimetric Density in Carbon Aerogels” 209th Meeting of the Electrochemical Society, **2006**, Abs. 877.