

Carbon Aerogels for Hydrogen Storage

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DOE Hydrogen Program

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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

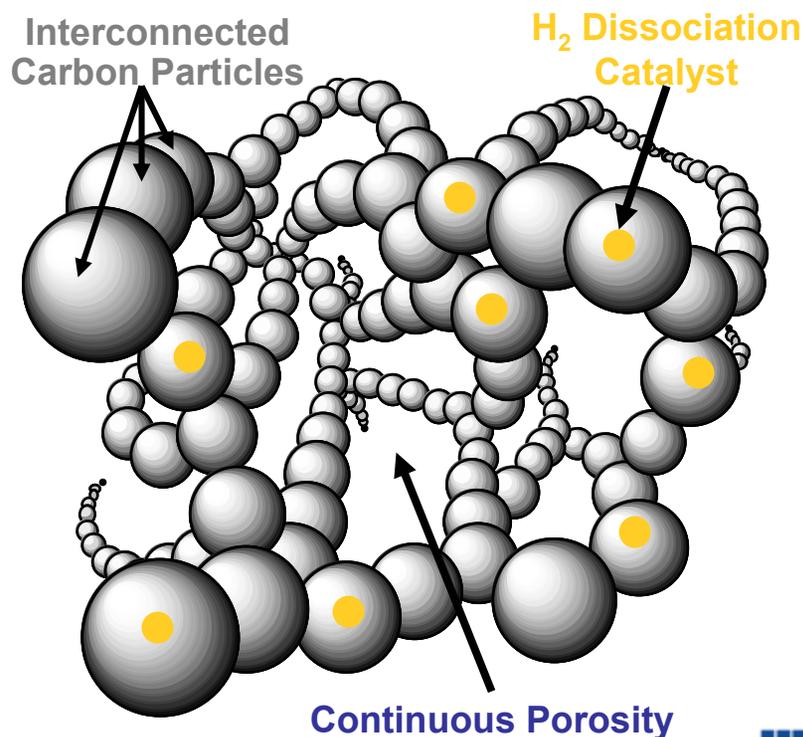
FY09

- Mechanistic Studies
- Reversibility/Lifetime Studies for CA Sorbent and Scaffolds



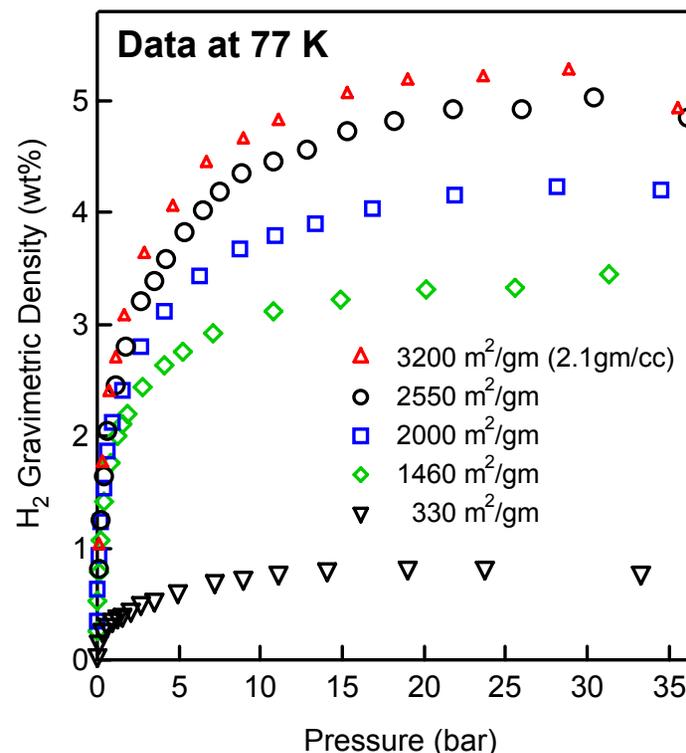
Project Approach

- Our approach is to utilize the flexibility of CA synthesis for the design 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



Kabbour, Baumann, Satcher, Saulnier and Ahn, *Chem. Mater.* **2006**, 18, 6085.



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 atomic layer deposition (ALD)³**

¹Baumann *et al.*, *Langmuir* **2002**, *18*, 7073; *Chem. Mater.* **2003**, *15*, 3745; *Langmuir* **2005**, *21*, 2647; *Langmuir* **2007**, *23*, 5161. US Patent 6613809.

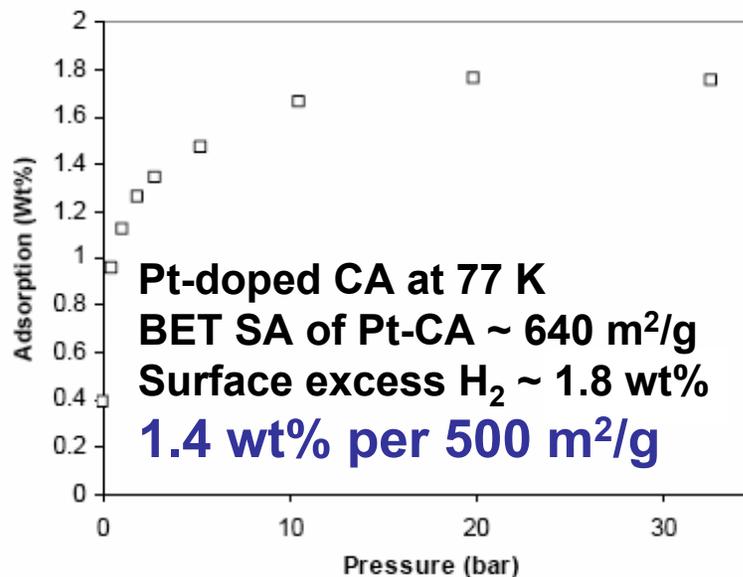
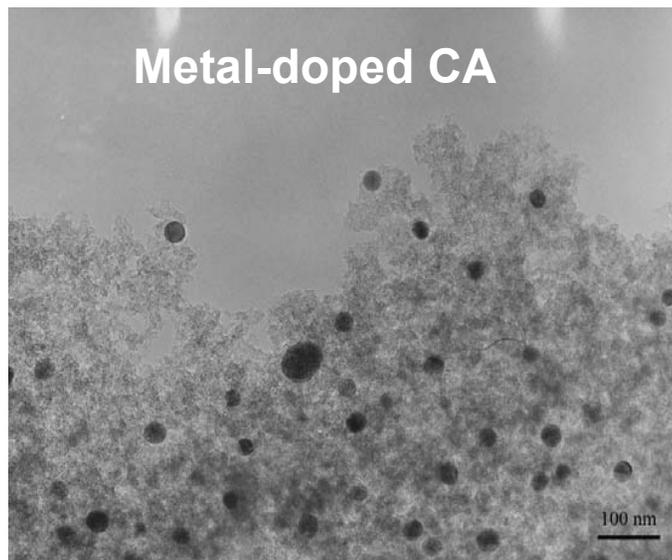
²Yang *et al.*, *J. Phys. Chem. C* **2007**, *111*, 11086, *JACS* **2006**, *128*, 8136.

³Baumann *et al.*, *Chem. Mater.* **2006**, *18*, 6106; *Nanotechnology* **2007**, *18*, 055303, *Langmuir* **2008**, *24*, 943.



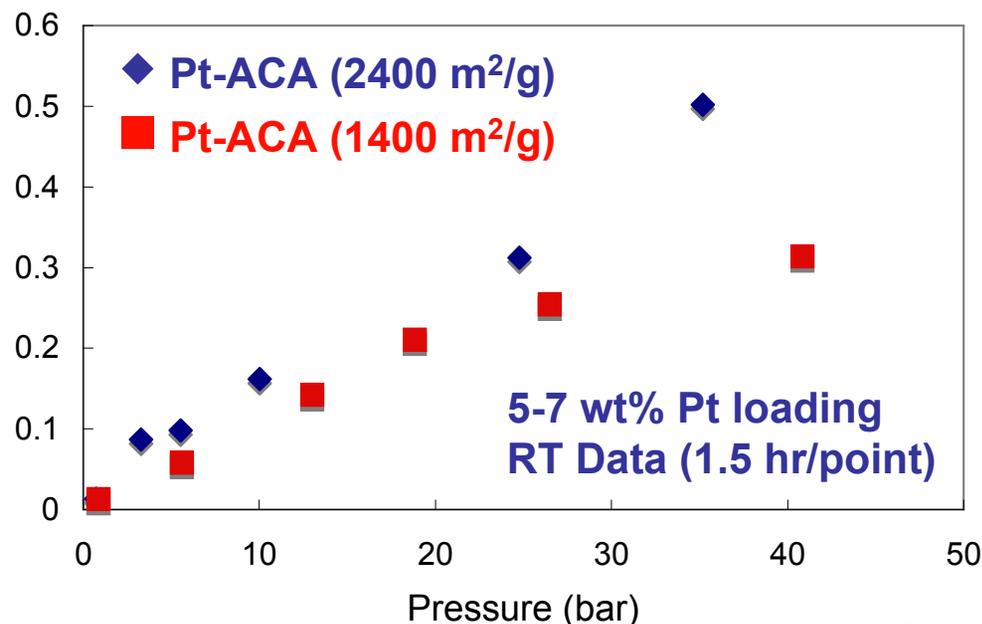
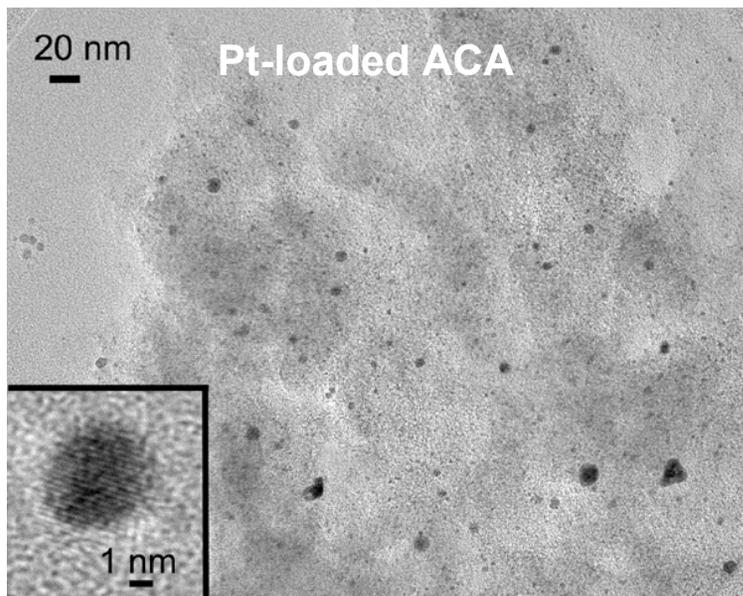
Technical Accomplishments: H₂ Sorption in Metal-doped CAs

- 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)



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

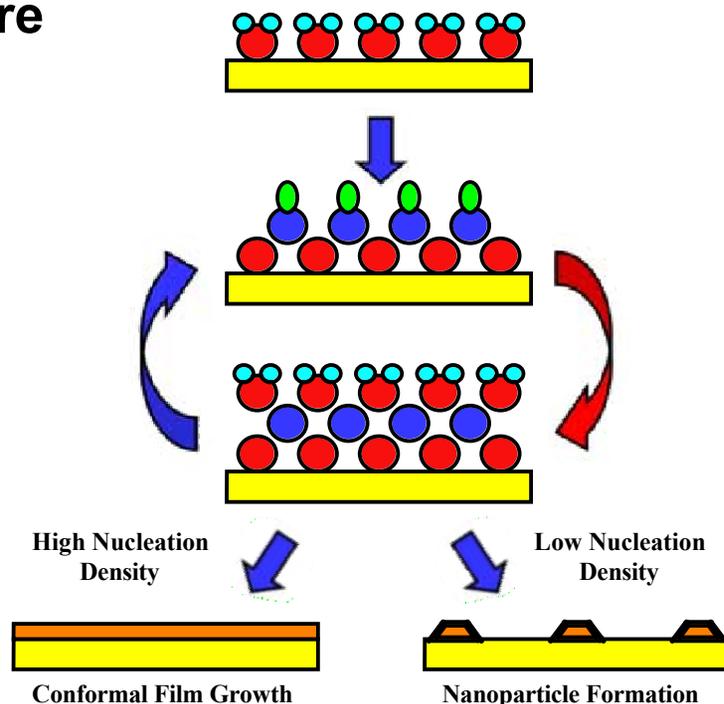


Technical Accomplishments: Atomic Layer Deposition on CAs

- 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

¹Leskala et al., *Thin Solid Films* **2002**, 409, 138.

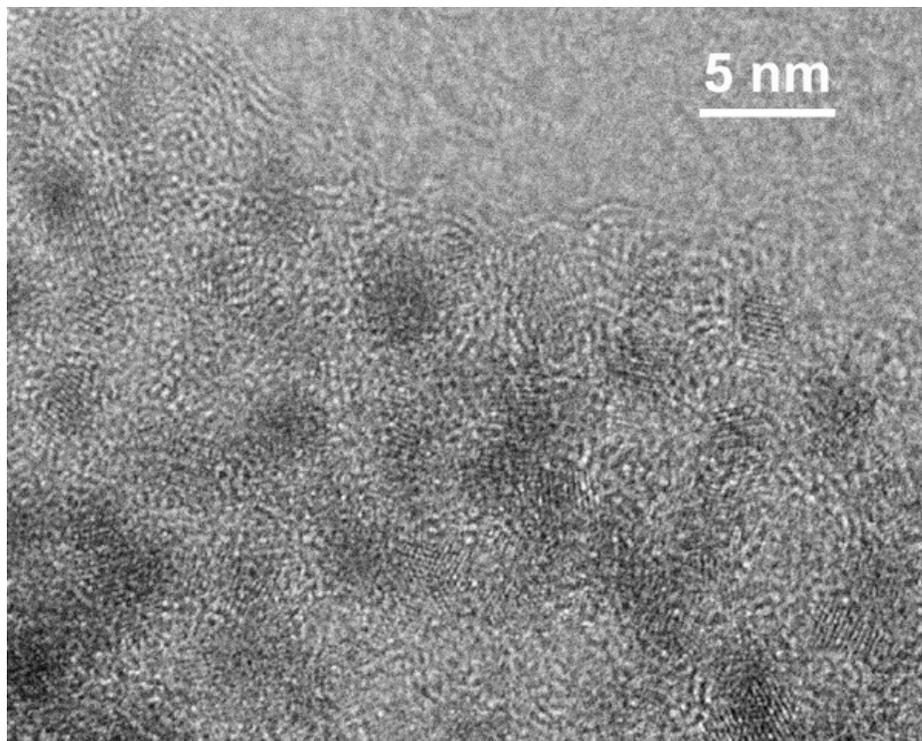
²Baumann et al., *Chem. Mater.* **2006**, 18, 6106; Biener et al., *Nanotechnology* **2007**, 18, 055303; Kucheyev et al., *Appl. Phys. Lett.* **2005**, 86, 083108, *Langmuir* **2008**, 24, 943.



Technical Accomplishments:

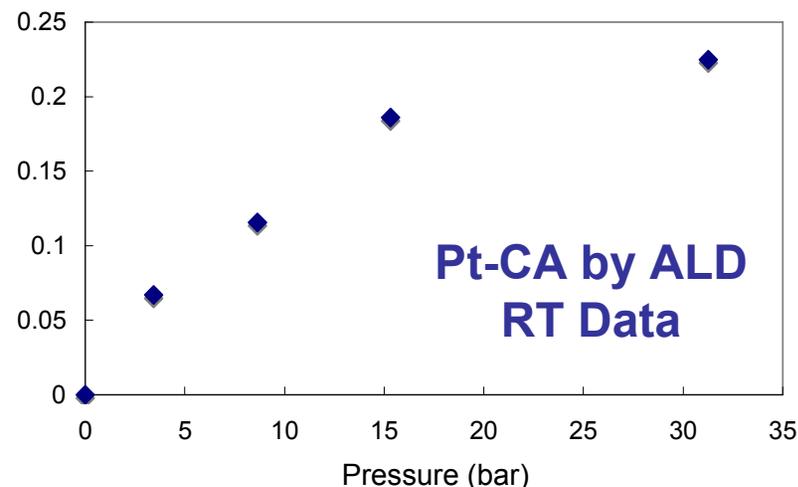
Pt ALD on CAs

- 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)



Technical Accomplishments: CAs as Scaffolds for Metal Hydrides

- 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



¹Previously demonstrated with NH_3BH_3 in SiO_2 : Autrey et al., *Angew. Chem. Int. Ed.* **2005**, 44, 3578.

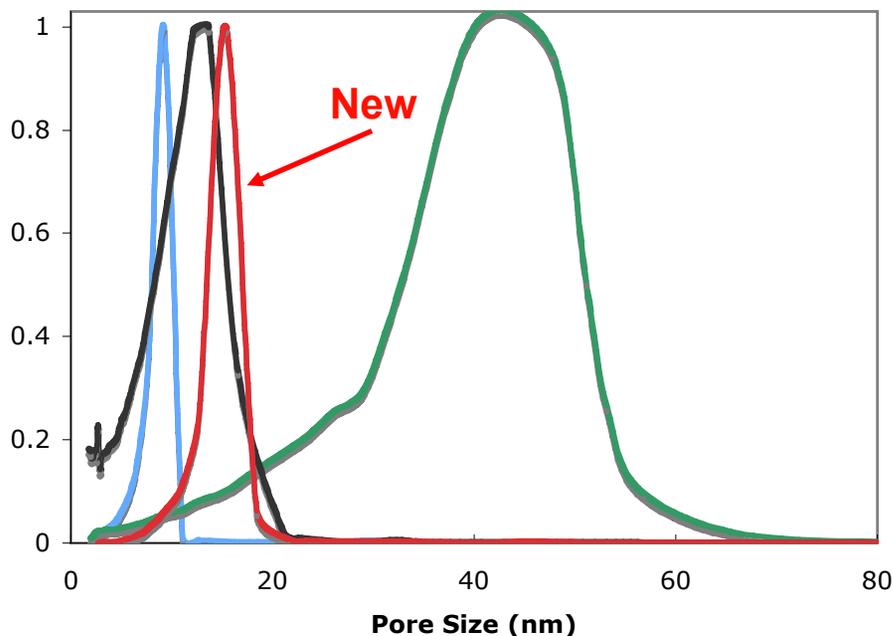
²de Jong et al., *Angew. Chem. Int. Ed.* **2006**, 45, 3501; de Jong et al, *Chem. Mater.* **2007**, 19, 6052.

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 cm³/g

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

Previous LLNL CAs
APD ~ 9.5 nm
PV = 1.1 cm³/g

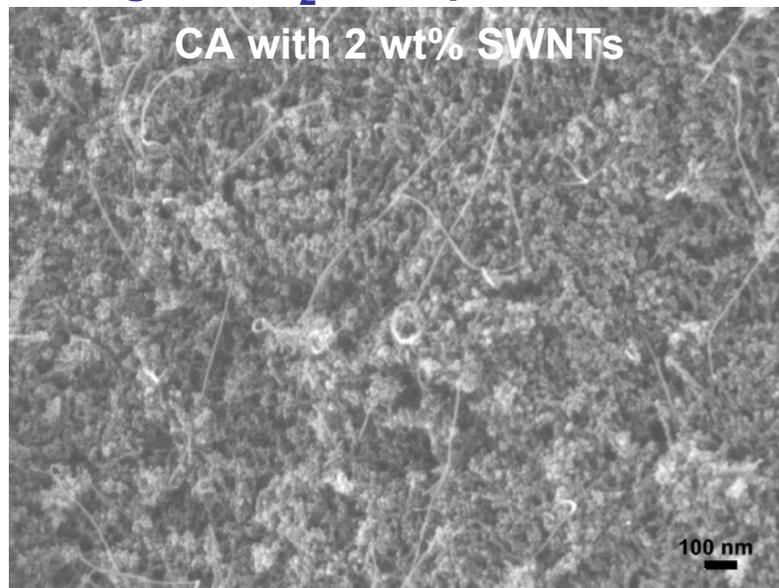
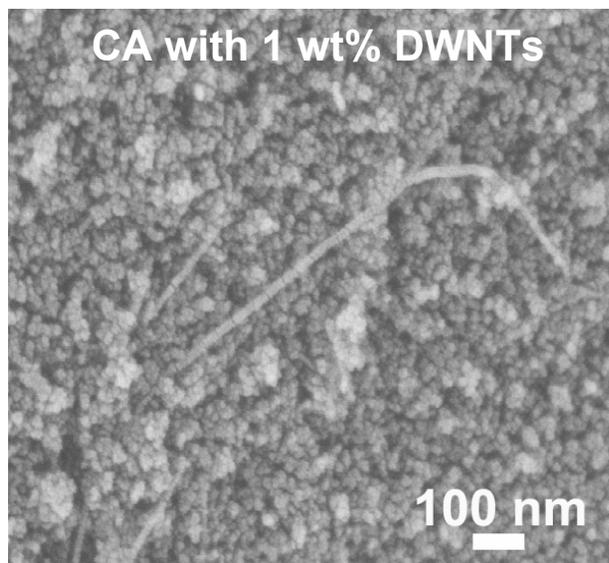
APD ~ 40 nm
PV = 2.7 cm³/g

- CA with small pore sizes (< 5 nm) delivered to NIST (Jack Rush) for LiBH₄ study



Technical Accomplishments: New CAs Scaffolds

- 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 H₂ 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

M. A. Worsley, J. H. Satcher, Jr. and T. F. Baumann, *Langmuir.*, 2008, *submitted*.



Future Work

- **Evaluation of RT H₂ uptake in metal-doped CAs:**
 - Utilize ALD for improved dispersion of catalysts (FY08)
 - Investigate alternative H₂ 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 H₂ 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 H₂ 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 H₂ uptake kinetics using atomic layer deposition
- Prepared new CA nanocomposites as scaffolds for metal hydride systems

Center Collaborations:

- Prof. Channing Ahn (CalTech): H₂ sorption measurements
- Craig Brown (NIST): Characterization of activated CA structure by NS techniques
- Prof. Yue Wu (UNC): Characterization of CA structure and H₂ 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

Storage Parameter	Units	2010 System Target	FY07 CA Material Results	FY08 CA Material Results
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt% H ₂)	5.3 wt% at 77 K and 30 bar ¹	1.2 wt% at RT and 100 bar ²
Energy Density	kWh/L (g H ₂ /L)	1.5 (45 g H ₂ /L)	~29 g H ₂ /L	TBD

¹Undoped CA with BET surface area ~3100 m²/g

²High surface area CA (~2400 m²/g) doped with Pt (6 wt%)

