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# Carbon Aerogels for Hydrogen Storage

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**Hydrogen Sorption Center of Excellence**  
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**ST-6**

This presentation contains no confidential or proprietary information

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# Overview of Project



## Timeline

- Project start: FY05
- Project end date: FY09
- Percent complete: 50%

## Budget

- Total project funding (proposed): \$1050K
- Funding received in FY06: \$265 K
- Funding for FY07: \$390 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)
  - H<sub>2</sub> 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



DOE Hydrogen Program

- 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 H<sub>2</sub> storage
- Optimization of the CA structure to maximize gravimetric and volumetric density in these materials:
  - High Surface Area (gravimetric density)
  - Control Porosity (volumetric density)
- Incorporation of dopants, such as boron or metal nanoparticles, into CAs to increase H<sub>2</sub> binding energy (> 10 kJ/mol):
  - Enhanced Binding Energy<sup>1</sup>
  - Catalytic Effects<sup>2,3</sup>

FY06

- Undoped CA Synthesis
- Evaluation of H<sub>2</sub> Sorption

FY07

- Dopant Incorporation
- Refine Materials Design

FY08

- Mechanistic Studies
- Reversibility/Lifetime Studies

<sup>1</sup>Zhang *et al.*, *Phys. Rev. Lett.* **2006**, 96, 016102.

<sup>2</sup>J. Schwarz, **1988**, U.S. patent 4,716,736. <sup>3</sup>Yang *et al.*, *Langmuir* **2005**, 21, 11421.

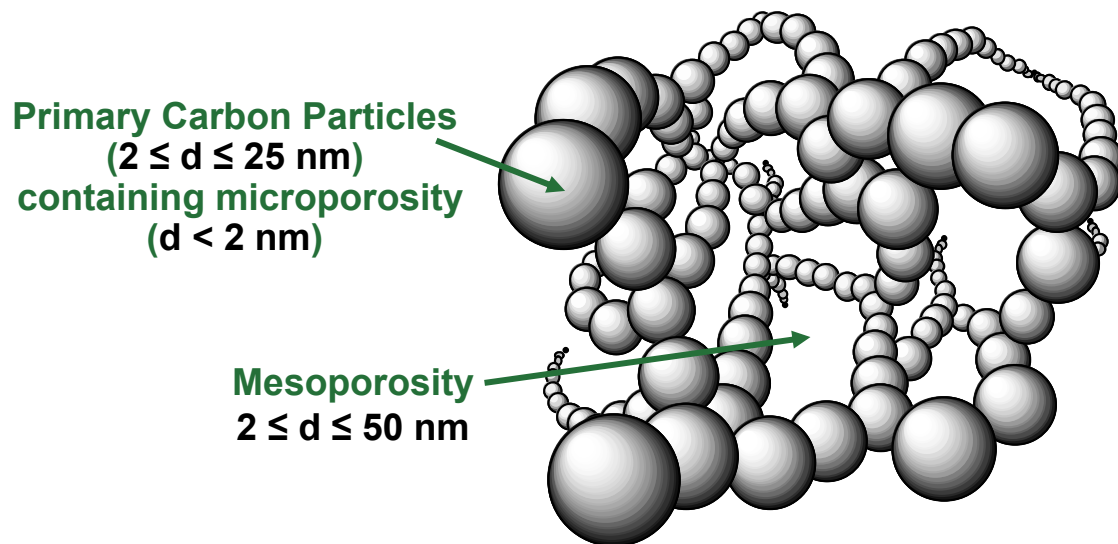


# Project Approach



DOE Hydrogen Program

- **CAs are unique porous materials comprised of 3D networks of interconnected nanometer-sized carbon particles:**



## CA Properties:

- Continuous porosities
- High surface areas
- Ultrafine cell/pore sizes
- Variable densities

- **CAs present a number of advantages for H<sub>2</sub> storage:**
  - Carbon aerogels can be inexpensively prepared in large quantities (multiple gram lots) as either monoliths or powders
  - Bulk properties of the carbon aerogel (density, surface area, pore size, pore volume) are controlled through synthetic parameters
  - Synthesis process allows for the homogeneous incorporation of dopants, such as boron or metal nanoparticles, into the CA matrix

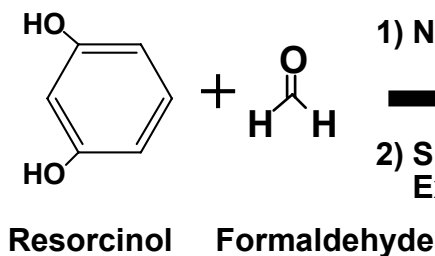


# Background on CA Synthesis



DOE Hydrogen Program

- CAs are prepared using sol-gel chemistry:

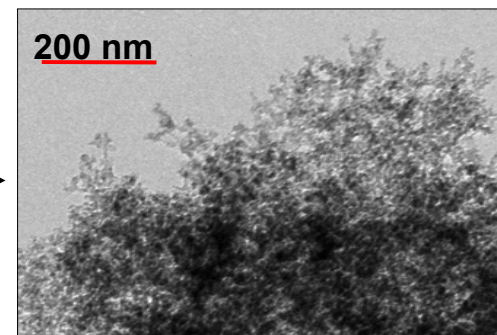
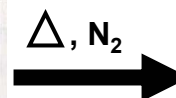


1)  $\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$   
2) Supercritical Extraction



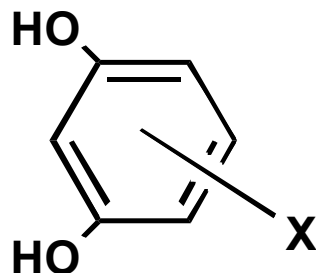
RF Organic Aerogel

Pekala, *J. Mater. Sci.* **1989**, *24*, 3221.

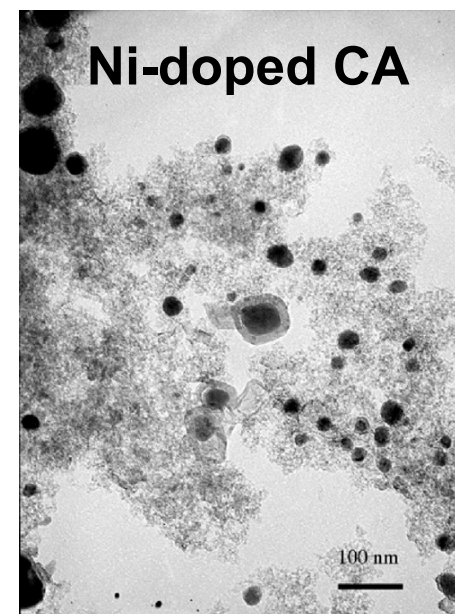


Carbon Aerogel

- Dopants (metals or boron) can be incorporated into the CA structure through the use of functionalized sol-gel precursors:



Where X is a metal ion binding site  
or a boron-containing unit



Baumann *et al.*, *Langmuir* **2002**, *18*, 7073; *Chem. Mater.* **2003**, *15*, 3745; *J. Non-Cryst. Solids* **2004**, *350*, 120; *Langmuir* **2005**, *21*, 2647; US Patent 6613809.

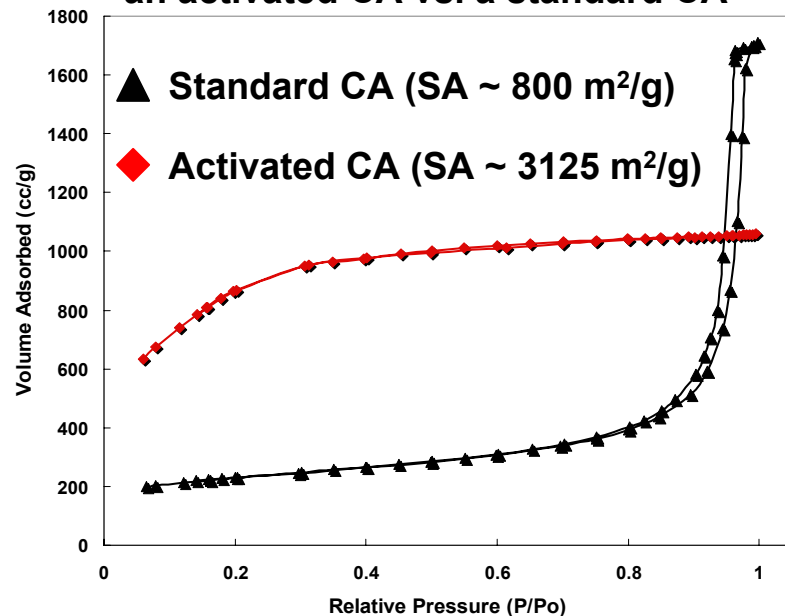
# Technical Accomplishments: High Surface Area CAs

- We have prepared new high surface area CAs through activation with CO<sub>2</sub>:
  - BET SA of 3200 m<sup>2</sup>/g is the highest value ever reported for CAs
  - CAs remained monolithic following activation
  - Increase in surface area tracks with activation time
  - Activated CAs are essentially microporous as opposed to traditional mesoporous CAs

Material	Time (h)	Mass Loss	BET SA (m <sup>2</sup> /g)
CA	—	—	390
ACA	2	43%	~1500
ACA	3	60%	~2300
ACA	4	70%	~2450
ACA	5	75%	~2800
ACA	6	85%	~3200

Activation Temperature: 950°C

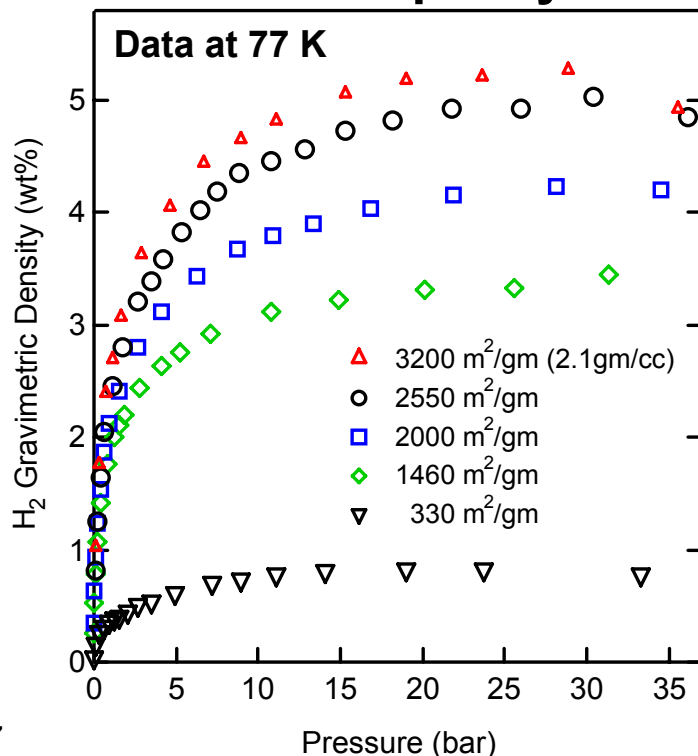
N<sub>2</sub> adsorption/desorption isotherms for an activated CA vs. a standard CA





# Technical Accomplishments: H<sub>2</sub> Adsorption in Activated CAs

- Surface excess H<sub>2</sub> adsorbed at 77K varies linearly with SA for activated CAs with SA up to ~2500 m<sup>2</sup>/g
- Activated CAs with higher SAs exhibited a break from “Chahine rule”
- Hydrogen uptake in the activated CAs was reversible
- The volumetric capacity for the 5.3 wt% material is 29.2 g H<sub>2</sub>/L



BET SA (m <sup>2</sup> /g)	H <sub>2</sub> (wt%) <sup>a</sup>	ΔH (kJ/mol) <sup>b</sup>
1460	3.5	6.7
2000	4.2	6.4
2500	5.0	6.4
3200	5.3	6.2

<sup>a</sup>Saturation value measured at 77K and 30 bar

<sup>b</sup>Low pressure measurement at 77K and 0 to 2.5 bar

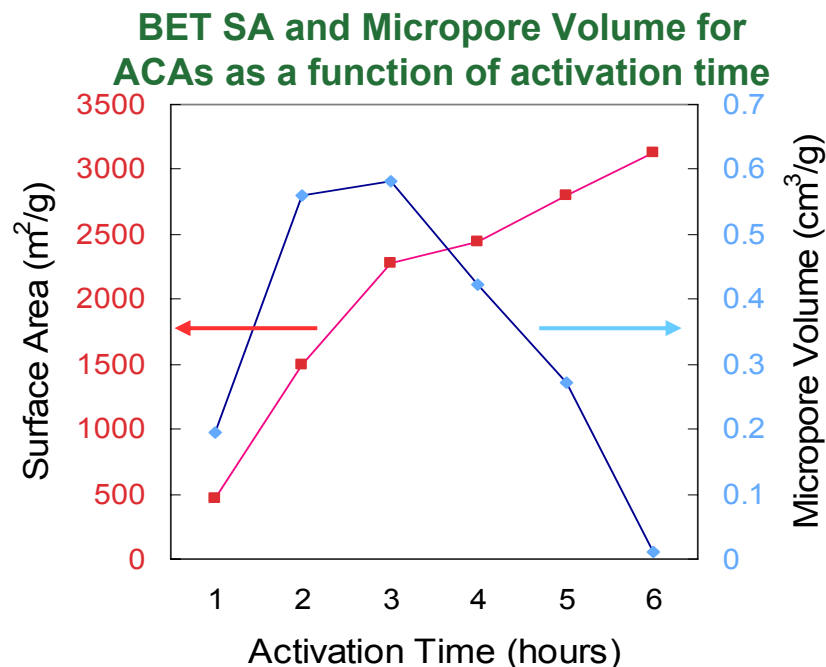
Kabbour, Baumann, Satcher, Saulnier and Ahn, *Chem. Mater.* **2006**, *18*, 6085.





# Technical Accomplishments: Structure Evolution in Activated CAs

- To further optimize these materials for H<sub>2</sub> adsorption, we are developing a better understanding of structure evolution in the activated CAs:
  - Changing porosity (micro- vs. mesopores) and surface properties (defects, radicals, oxygen, etc) during the activation process
- We are currently characterizing the activated CA microstructure using <sup>129</sup>Xe NMR, EPR, USAXS, neutron scattering and soft X-ray techniques
- Hydrogen adsorption results for the activated CAs emphasize the importance of *controlling pore size* in the design of new H<sub>2</sub> adsorbants



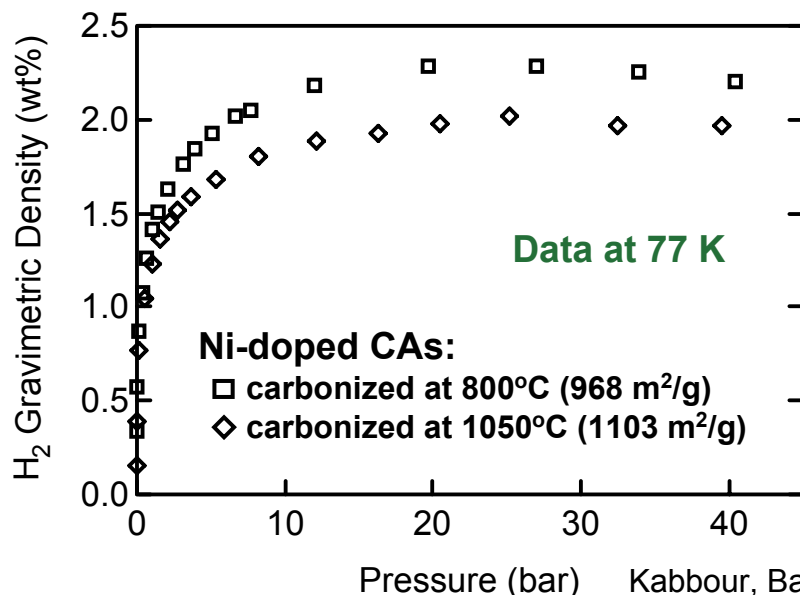
Baumann *et al. Carbon*, 2007, submitted.





# Technical Accomplishments: H<sub>2</sub> Adsorption in Metal-doped CAs

- We prepared a series to metal-doped CA with the goal of altering H<sub>2</sub> sorption enthalpy in these materials
- Incorporation of metal nanoparticles (Ni, Co) into the *unactivated* CAs appears to alter sorption enthalpy:
  - Higher H<sub>2</sub> gravimetric density observed in the lower surface area Ni-doped CA material (Metal-H<sub>2</sub> interactions? Modified carbon structure?)
  - Enhanced sorption enthalpies relative to undoped CAs
- Activation of these metal-doped CAs has been problematic



C Temp (°C)	BET SA (m <sup>2</sup> /g)	H <sub>2</sub> (wt%) <sup>a</sup>	ΔH (kJ/mol) <sup>b</sup>
Ni-800	970	2.3	7.0
Ni-1050	1100	2.0	7.1
Co-800	980	2.0	7.5

<sup>a</sup>Saturation value measured at 77K and 30 bar

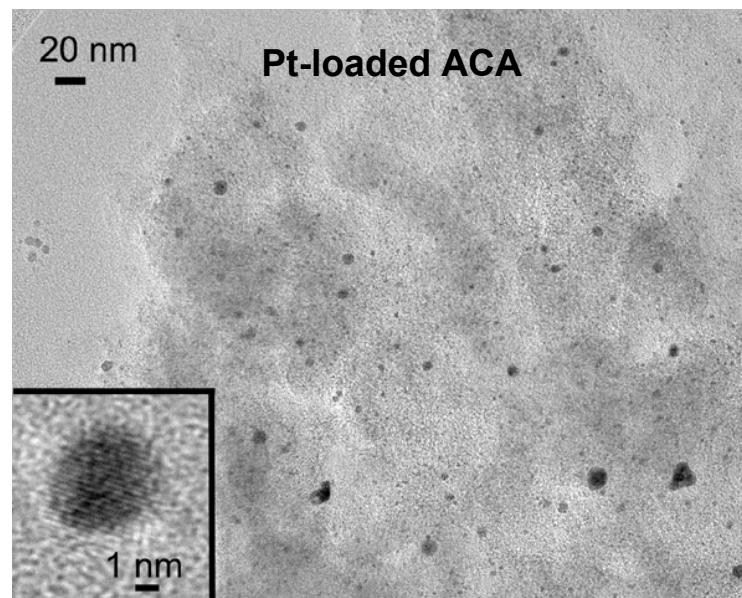
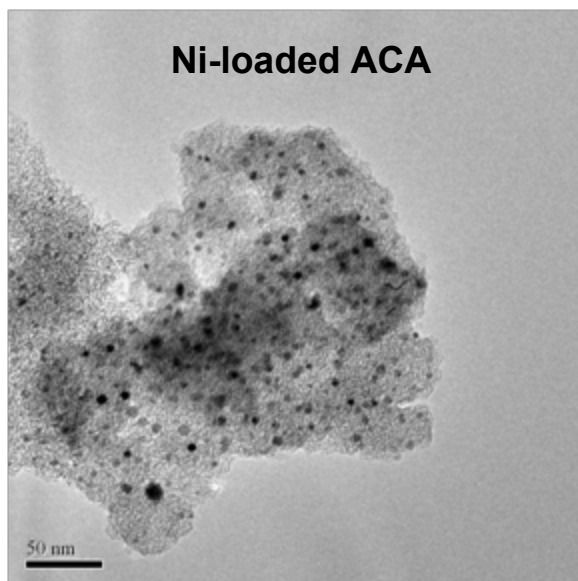
<sup>b</sup>Low pressure measurement at 77K and 0 to 2.5 bar

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



# Technical Accomplishments: Metal-loading of Activated CAs

- Since the presence of metals complicates activation process, we are incorporating metal dopants after activation through an impregnation process:
  - Activated CAs (2000 m<sup>2</sup>/g) have been treated with metal salts (Ni(NO<sub>3</sub>)<sub>2</sub> or H<sub>2</sub>PtCl<sub>6</sub>) that are subsequently reduced with H<sub>2</sub> to form metal nanoparticles

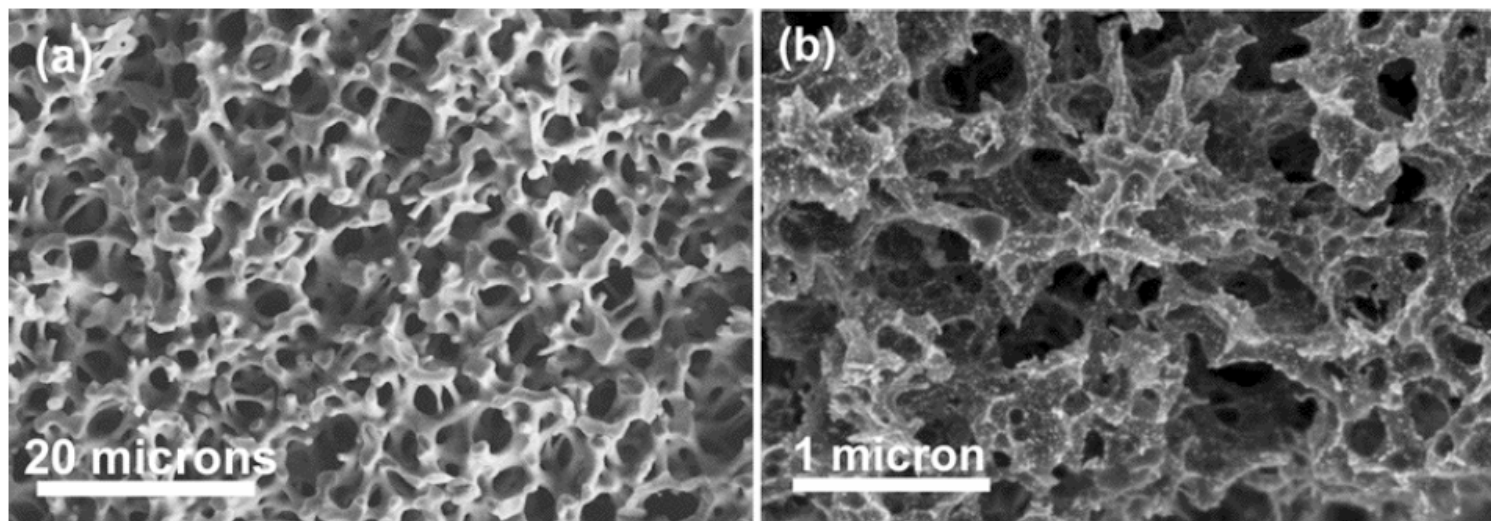


- We are still optimizing process conditions to control metal loading levels, distribution and nanoparticle sizes



# Technical Accomplishments: Atomic Layer Deposition on Activated CAs

- We are also investigating alternative methods for metal incorporation after activation:
  - **Atomic Layer Deposition<sup>1</sup>**: Self-limiting form of CVD that can be used to deposit metal nanoparticles into high aspect ratio structures, such as the porosity of aerogels<sup>2</sup>
  - This approach should allow for greater control over catalyst loading in CAs
  - We are currently using ALD to deposit Ni, Pd and Pt nanoparticles on the inner surfaces of CA materials



SEM images of CAs (a) before and (b) after treatment with Pt ALD

<sup>1</sup>Leskala et al., *Thin Solid Films* **2002**, 409, 138.

<sup>2</sup>Baumann et al., *Chem. Mater.* **2006**, 18, 6106; Biener et al., *Nanotechnology* **2007**, 18, 055303.



# Future Work

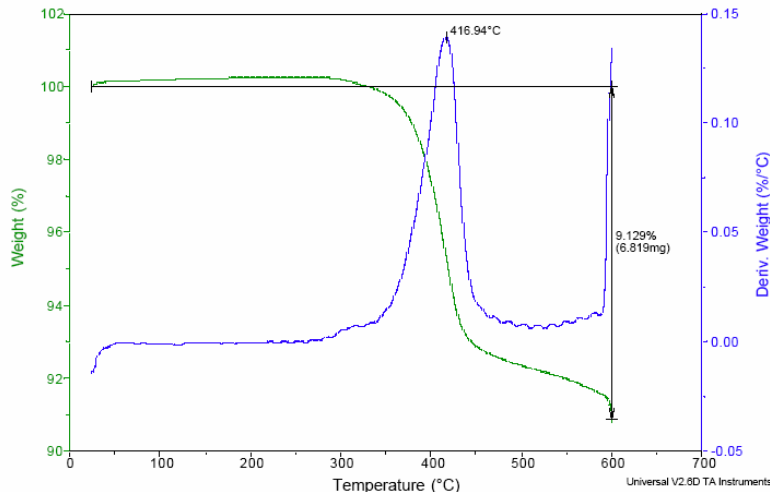


DOE Hydrogen Program

- **Current areas of focus:**
  - **Further optimization of the activated CA microstructure**
    - Understand evolution of porosity and surface properties during activation process (Why the break from “Chahine rule”?) (FY07)
    - Control of porosity (pore size, CA density) to further improve volumetric density (FY07)
  - **Incorporation of dopants into high surface area CAs**
    - Develop methods to introduce metals (Ni, Pd or Pt) into CAs after activation (FY07-08)
    - Evaluate H<sub>2</sub> adsorption and kinetics for metal-loaded CA (FY07-08)
    - Boron has also been incorporated into CA network through B-functionalized sol-gel precursors (FY08)
- **New Direction:**
  - **Utilization of CAs as scaffolds for metal hydride systems**
    - Work with the HRL Group (MHCoE)

# Technical Accomplishments: CAs as Scaffolds for Metal Hydrides

- We are fabricating CAs as scaffolds for metal hydrides with the HRL group (MHCoeE)
- Nanoporous scaffolds can improve kinetics of metal hydrides by limiting particle size and reducing diffusion distances<sup>1</sup>
- Our focus has been on engineering CA porosity to minimize capacity penalty (gravimetric and volumetric) associated with the use of the scaffold



- Melt infusion of  $\text{LiBH}_4$  into CA with high pore volume ( $\sim 2.7$  cc/g)
- CA/ $\text{LiBH}_4$  composite gave  $\sim 8\%$   $\text{H}_2$  by weight
- Decrease in  $\text{H}_2$  desorption temperature versus bulk  $\text{LiBH}_4$

- Reversibility in the composite was poor, likely due to particle coarsening during cycling (issue with pore size?)

<sup>1</sup>Previously demonstrated with  $\text{NH}_3\text{BH}_3$  in  $\text{SiO}_2$ : Autrey et al., *Angew. Chem. Int. Ed.* 2005, 44, 3578.



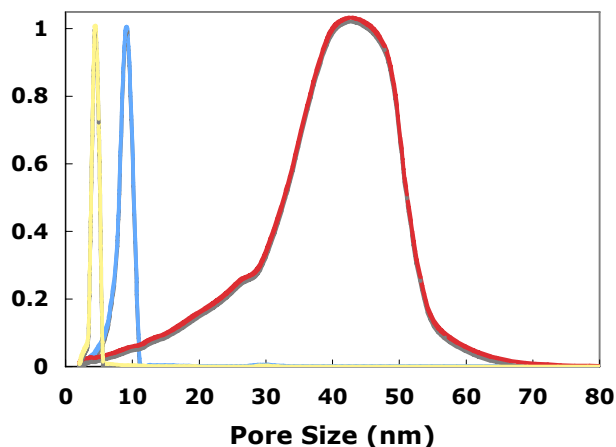


# Future Work: CAs as Scaffolds for Metal Hydrides



- Current focus to improve the performance of CA scaffolds includes:

- Control of pore size distribution in CAs (FY07)



— High Pore Volume CA  
PV = 2.7 cc/g, APD ~ 40 nm

— Intermediate CA  
PV = 1.1 cc/g, APD ~ 9.2 nm

— Low Pore Volume CA  
PV = 0.5 cc/g, APD ~ 4.5 nm



- Modification of CA surface chemistry to change wetting behavior of metal systems (FY07-08)
- Incorporation of destabilizing agents and catalysts into the CA framework (FY08)
- Explore the potential of inorganic aerogel scaffolds such as  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  (FY08)



# Project Summary



DOE Hydrogen Program

**Relevance:** Design of new CA materials for hydrogen storage

**Approach:** Incorporation of dopants into high surface area CA to maximize H<sub>2</sub> uptake and modify binding energies

## **Technical Accomplishments:**

- Prepared and characterized new class of activated CAs with surface areas as high as 3200 m<sup>2</sup>/g
- ACA with surface area ~3200 m<sup>2</sup>/g exhibited gravimetric H<sub>2</sub> density of 5.3% at 77 K (29.2 g H<sub>2</sub>/L)
- Incorporated metal dopants (Ni and Pt) into these high surface area ACAs
- Prepared high PV CAs as scaffolds for metal hydride systems

## **Center Collaborations:**

- Prof. Channing Ahn (CalTech): H<sub>2</sub> sorption measurements
- Craig Brown (NIST): Characterization of activated CA structure by NS techniques
- Prof. Yue Wu (UNC): Characterization of CA structure and H<sub>2</sub> uptake by advanced NMR techniques
- John Vajo (HRL, MHCoe): CA scaffolds for metal hydrides





# Summary for CA Materials



DOE Hydrogen Program

## DOE On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 System Target	FY06 CA Material Results <sup>a</sup>	FY07 CA Material Results <sup>a</sup>
Specific Energy	kWh/kg (wt% H <sub>2</sub> )	2.0 (6 wt% H <sub>2</sub> )	4 wt%	5.3 wt% <sup>b</sup>
Energy Density	kWh/L (g H <sub>2</sub> /L)	1.5 (45 g H <sub>2</sub> /L)	~22 g H <sub>2</sub> /L	~29 g H <sub>2</sub> /L <sup>c</sup>
Sorption Enthalpy	kJ/mol	10 to 50	6 kJ/mol	7.5 kJ/mol <sup>d</sup>

<sup>a</sup>Data for CA material only, not system value

<sup>b</sup>Data for an undoped CA (SA~3200 m<sup>2</sup>/g) collected at 77 K and 30 bar

<sup>c</sup>Calculated for a CA with *monolithic* density ~0.55 g/cm<sup>3</sup>

<sup>d</sup>Co-doped CA carbonized at 800°C