Metal-doped Carbon Aerogels for Hydrogen Storage

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Overview of Project

**Timeline**
- Project start: FY05
- Project end date: FY07
- Percent complete: N/A

**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

**Budget**
- Total project funding
  - DOE share
  - Contractor share
- Funding for FY04: N/A
- Funding for FY05: $240K

**Partners**
- Prof. Mildred Dresselhaus-MIT
  - Materials Characterization
- Dr. Greg Exarhos-PNNL
  - Advanced NMR analysis
Project Objectives

• To develop new nanostructured carbon materials that meet the targets set by DOE for hydrogen storage:

  • Novel metal-doped carbon aerogels (MDCAs) will be prepared, characterized and evaluated for their hydrogen storage properties

  • Mechanisms associated with hydrogen physisorption and chemisorption in these carbon-based materials will be investigated using advanced nuclear magnetic resonance (NMR) techniques

• Insights gained from MDCA systems should also be beneficial to the other nanostructured carbon systems, leading to the design of an optimized carbon-based material for hydrogen storage
Technical Approach

- Metal-doped CAs possess desirable structural features for the investigation of hydrogen uptake and release:

  **Graphitic Nanostructures**
  - Nanoporosity
  - Curved surfaces for increased adsorption potential

  **Mesoporosity**
  - \(2 \leq d \leq 50\) nm
  - High Surface Areas
  - Provides accessibility

**Metal Nanoparticles**
- \(d = 5\) to 60 nm
- Catalyze the formation of graphitic structures

**Primary carbon particles**
- \(d = 2\) to 20 nm
- Amorphous or Graphitic?
- Contain microporosity

**Metal-doped CAs** can be readily prepared in bulk quantities (gram scale)
Background on Carbon Aerogels

- **Novel mesoporous materials:**
  - Low mass densities (0.5-0.01 g/cm³)
  - High surface areas (400-1000 m²/g)
- **Prepared using sol-gel chemistry:**

  \[
  \text{Resorcinol} + \text{Formaldehyde} \\
  \begin{array}{c}
  1) \text{Na}_2\text{CO}_3, \text{H}_2\text{O} \\
  2) \text{Supercritical Extraction}
  \end{array} \\
  \rightarrow \text{RF Organic Aerogel} \\
  \rightarrow \text{1050°C, } \text{N}_2 \rightarrow \text{Carbon Aerogel}
  \\
  \text{Density (g/cm³)} \\
  \text{RF} 0.106 \\
  \text{RF} 0.411 \\
  \text{CA} 0.149 \\
  \text{CA} 0.637
  \\
  \text{H}_2 \text{ (wt%)} \\
  \text{RF} 16.7 \\
  \text{RF} 4.4 \\
  \text{CA} 5.8 \\
  \text{CA} 3.2
  \\
  \text{H}_2 \text{ (kg/m³)} \\
  \text{RF} 21.3^* \\
  \text{RF} 19.3 \\
  \text{CA} 9.3 \\
  \text{CA} 21.0

- **H₂ storage properties of undoped CAs have been investigated:**
- **Flexibility of organic sol-gel chemistry can be exploited to improve H₂ storage capacity in carbon aerogels**

  Measurements were performed at 77 K, *1000 psi
  (Pekala et al. 1995, UCRL-JC-120315)
Current Technical Status

FY05 Accomplishments:

1. Preparation of MDCAs:
   - Different metals: Co, Ni, Fe (~8-10 wt% M-loading)
   - Different densities: 200 mg/cc, 400 mg/cc
   - Different carbonization temperatures: 800°C, 1050°C

2. Structural characterization:
   - SEM, TEM, XPS, and XRD (Collaboration with Dresselhaus Group at MIT)
   - Examining carbon structure in MDCAs using solid state $^{13}$C NMR techniques
   - Currently using $^{129}$Xe NMR experiments to probe textural porosity (LLNL/PNNL Collaboration: *J. Am. Chem. Soc.* 2004, 126, 5052)
Current Technical Status

• Incorporation of metal species into aerogel framework using sol-gel precursors containing ion exchange sites:
  • General technique that can be used to incorporate a variety of metals

![Chemical Reaction Diagram]

• Physical Properties:
  • Density Ranges: 150-400 mg/cm³
  • Surface Areas: 500-900 m²/g
  • Metal Content: 1-10% by weight

• Metal nanoparticles form during carbonization (5 to 60 nm)

Current Technical Status

- Formation of graphitic nanostructures in our MDCAs (M = Co, Ni, Fe) observed at relatively low carbonization temperatures
  - XPS data show metal nanoparticles coated with graphitic carbon
  - Potential substrates for the growth of carbon nanotubes

Co-doped CA ($T_c = 1050^\circ\text{C}$)

LLNL Sol-Gel Synthesis Facilities

• **Laboratory Space:**
  5 Labs totaling ~3000 ft²

• **Equipment:**
  2 Rapid Super Critical Extractors
  20L High Temperature Extractor
  16L CO₂ Extractor
  10 Polaron CO₂ Extractors
  5 Lindberg Tube Furnaces
  Programmable Sintering Furnaces
  High Temp Vacuum Furnace
  Clean Room
  Quench Furnace
  Glove Box
Current Technical Status

• **Solid state NMR techniques will be used to:**
  
  • Determine the nature of metal-carbon, carbon-hydrogen and metal-hydrogen interactions utilizing *in-situ* $^1$H, $^2$H, $^1$H-$^{13}$C and $^1$H-M (where M = $^{59}$Co, $^{61}$Ni, $^{57}$Fe, $^{11}$B and $^{27}$Al) NMR
  
  • Determine the mode of hydrogen interaction with the MDCAs

• **These experiments will allow us to assess the most favorable combinations of carbon-metal-hydrogen and relevant structural motifs for optimal hydrogen storage**

• **We are currently using NMR methods to examining the structure and dynamics of H$_2$ storage in alanate systems (collaboration with SNL)**
LLNL NMR Facilities

• LLNL has state of the art NMR facilities that compliment those at UNC:
  • Multiple field strengths (20, 42, 82, 300, 400, 500, 600 MHz)
  • Full suite of solids and liquid state NMR probes
  • Field gradients for diffusion and imaging experiments
  • OP $^{129}$Xe capabilities
  • Cryostats capable of reaching 4K and transmission line probes for observation of in-situ H$_2$ adsorption
  • Extensive experience in the characterization of disordered materials, double resonance SEDOR experiments, and dynamics
Future Work

Remainder of FY05:

- **Evaluate $H_2$ storage properties for MDCAs:**
  - Currently constructing apparatus for volumetric $H_2$ measurements
- **Initiate mechanistic studies using advanced NMR techniques
- **Milestones:**
  1) Down-select number of MDCAs examined
  2) Optimize $H_2$ storage capacities for most promising candidates through modification of:
     - Metal species (type, doping level)
     - Carbonization temperature (degree of graphitization)
     - Particle size (surface area, pore size distribution)
     - Density (weight, strength)

FY06 efforts:

- Determining reversibility and lifetime in these materials over multiple charge/discharge cycles
- Continue mechanistic studies using advanced NMR techniques
Hydrogen Safety for Effort

- The most significant hydrogen hazard associated with this project:
  - The use of compressed hydrogen gas in the evaluation of the MDCA materials
  - Volumetric hydrogen measurements will require the use of hydrogen gas in a pressure manifold
  - The NMR experiments will involve pressurizing quartz NMR tubes with hydrogen gas
Hydrogen Safety for Effort

- Our approach to deal with this hazard:
  - We have an integrated safety management (ISM) plan in place at LLNL for the use of hydrogen gas:
    - Personnel will have training in handling pressurized gases
    - The equipment will be tested by certified personnel to verify that all parts conform to ASME pressure standards
  - The experiments (both volumetric and NMR) will require small volumes of hydrogen gas, limiting the risk associated with this work
Overlap with Center Members

• Interaction with National Renewable Energy Laboratory (Heben/Dillon) for H₂ adsorption/desorption measurements:
  • Measure H₂ uptake/release for the MDCA samples
  • Performed initial TPD studies on our “baseline” un-doped CA materials

• Complement NMR work at UNC-Chapel Hill (Prof. Y. Wu) in the analysis of H₂ uptake and release in carbon-based materials
  • Evaluate mechanisms of interaction using NMR techniques
  • Unique capabilities at LLNL’s NMR Center

• Opportunities for developing computational effort
  • Models for growth of metal particles and graphitic nanostructures
  • Graphitic overcoat on metal nanocrystals
  • H₂ interaction with MDCAs