Hydrogen Storage in Graphite Nanofibers and the Spillover Mechanism
A Study Carried Out in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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This presentation does not contain any proprietary or confidential information
CbHS
Center of Excellence Partners

9 university projects (at 7 universities), 4 government labs, 1 industrial partner

- Univ of Michigan (H₂ spillover and MOFs)
- Penn State (B-C-N materials)
- Univ North Carolina (nmr)
- Duke Univ (Nanocluster seeds)
- Rice University (carbon nanotubes, theory)
- CalTech (Edge activation, polymers, measurement)
- NREL (Materials, theory, measurement, systems, center integration)
- Air Products (Materials, measurement, theory, engineering)
- Livermore (aerogels)
- Oak Ridge (Carbon nanohorns)
- Univ of Pennsylvania (polymers)

Steering Committee

Department of Chemical Engineering
Overview

Timeline
• Project start date: FY05
• Project end date: FY09
• New Start

Budget
• Expected Total Funding
  • DOE share: $939,356
  • Contractor share: $280,000
• Funding for FY05: $170,000

Barriers
• General
  • Weight & Volume
  • Efficiency
• Reversible Solid-State Material
  • Hydrogen Capacity & Reversibility
  • Lack of Understanding of H Physi- & Chemisorption

Partners
• Sample/adsorbed H Measurements and Characterization
  • NREL, NIST
Project Objectives

• To develop Graphite Nanofiber (GNF) based hydrogen storage materials with capacities in excess of 6 wt%  
  – To Optimize GNF Synthesis Catalyst & Pretreatment Conditions for Hydrogen Storage  
  – To Develop Bridge-Building Techniques for Spillover to Enhance Hydrogen Storage  
  – To Obtain a mechanistic understanding for hydrogen spillover in nanostructured carbon materials
Project Milestones

2009
- Optimized Synthesis, Pretreatment, Spillover
- 6.0 wt%

2008
- General Nanocarbon Bridge-Building Techniques
- 5.5 wt%

FY 2007
- GNF Bridge-Building Techniques
- 5.5 wt%

2006
- Mechanistic Spillover Model
- 4.5 wt%

2005
- 3.5 wt%

Hydrogen Capacity Deliverable (wt%)
Approach

• Development of GNF material with > 6 wt% reversible hydrogen capacity
  – Systematic studies of GNF synthesis catalysts (metal alloys) & pretreatment conditions
  – Production of composite materials containing catalysts to dissociate hydrogen
  – Enhancement & optimization of spillover mechanism through modeling & bridge-building techniques
Technical Accomplishments

- Development of Calibrated High Pressure Apparatus & Test Protocol
- Demonstration of Bridge-Building Technique to Enhance Spillover
- Screening of Two GNF-Metal Hydride Composites for Spillover Enhancement
- Identification of Carbon Composite Demonstrating Reversible Hydrogen Storage Capacity of 1.8 wt% at 298 K & 10 MPa
Low Pressure Spillover Enhancement

- AX-21 Receptor
- 5 wt% Pd/C Catalyst
- Carbon ‘bridge’ formed by carbonization of precursor (e.g., glucose)
- Adsorption at 298 K
- < 4% adsorbed volume at 0.1 MPa due to PdH$_{0.6}$
- Adsorption capacity tripled at 0.1 MPa (only doubled without bridges)

High Pressure Measurement

- Calibrated Volumetric System (LaNi$_5$ & TiAl$_{0.12}$V$_{0.04}$)
- In-situ Pretreatment to 1023 K (750 C)
- Adsorption Measurements to 12 MPa (1800 psia)

High Pressure Spillover Enhancement

- Extension of low-pressure work
- Identical trends observed at high pressure
- Completely reversible adsorption at 298 K
- Adsorption capacity tripled at 10 MPa (only 1.3 times without bridges)
- 1.8 wt% capacity at 10 MPa without optimization

Graphite Nanofiber-Metal Hydride Composites

- Herringbone GNF
- LaNi$_5$ & TiAl$_{0.12}V_{0.04}$ alloy powders 50 - 500 micron
- Incipient wetness-paste direct doping technique
- Isotherms are sum of individual component capacities
- No spillover at 298 K from these metal alloys
- Investigating catalysts & conditions to promote spillover

Future Work

• Remainder of FY 2005 (3.5 wt%)
  – Screen & select optimal GNF synthesis catalyst
  – Extend demonstrated bridge-building technique to GNF composite materials
  – Develop mechanistic understanding for spillover

• FY 2006 (4.5 wt%)
  – Optimize catalyst/pretreatment conditions
  – Optimize bridge-building conditions
  – Implement spillover to achieve target for storage
Addenda

- Slides after this page will not be on the poster, but will be part of the Annual Review CD material.
Hydrogen Safety

Primary Hydrogen Hazard

- Potential energy release & fire from hydrogen leaking at high pressure from measurement system

Secondary Hazards

- Issues related to the nature of hydrogen as a compressed gas (e.g. stored potential energy, asphyxiation)
Hydrogen Safety

Mitigation of Primary Hazard

• Use of high-integrity VCR® fittings in high pressure system (leak rate < $10^{-8}$ atm-cc/sec)
• Component pressure rating to 2000 psia
• Helium leak check at 1500 psia prior to hydrogen introduction
• Procedural control to evacuate sample for minimum 1 hr to remove air from system
• Backfill with helium prior to sample removal
• System volume < 50 cc & isolated during static measurements to limit leakage quantities