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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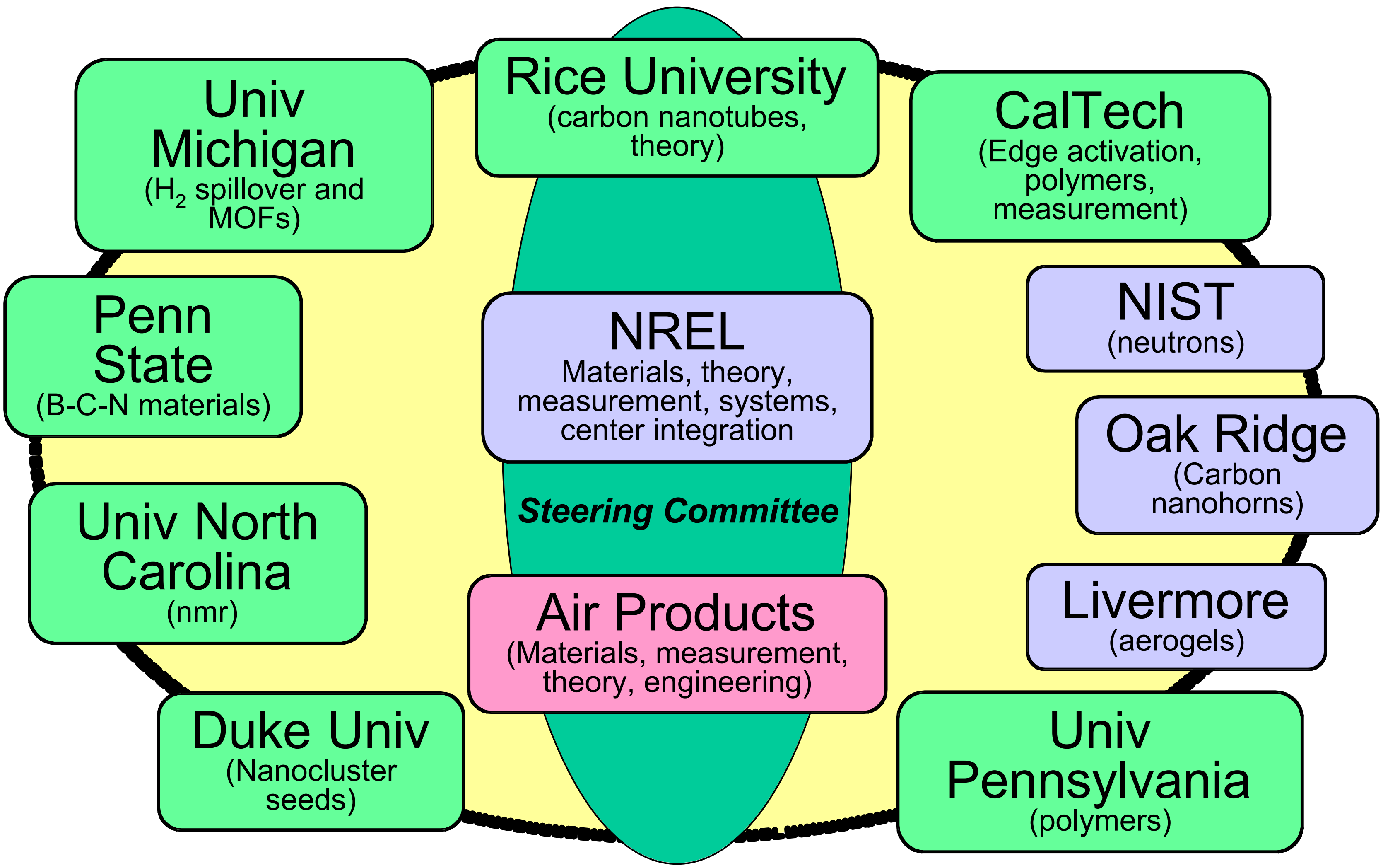
STP40

CbHS
Center of Excellence Partners

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



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

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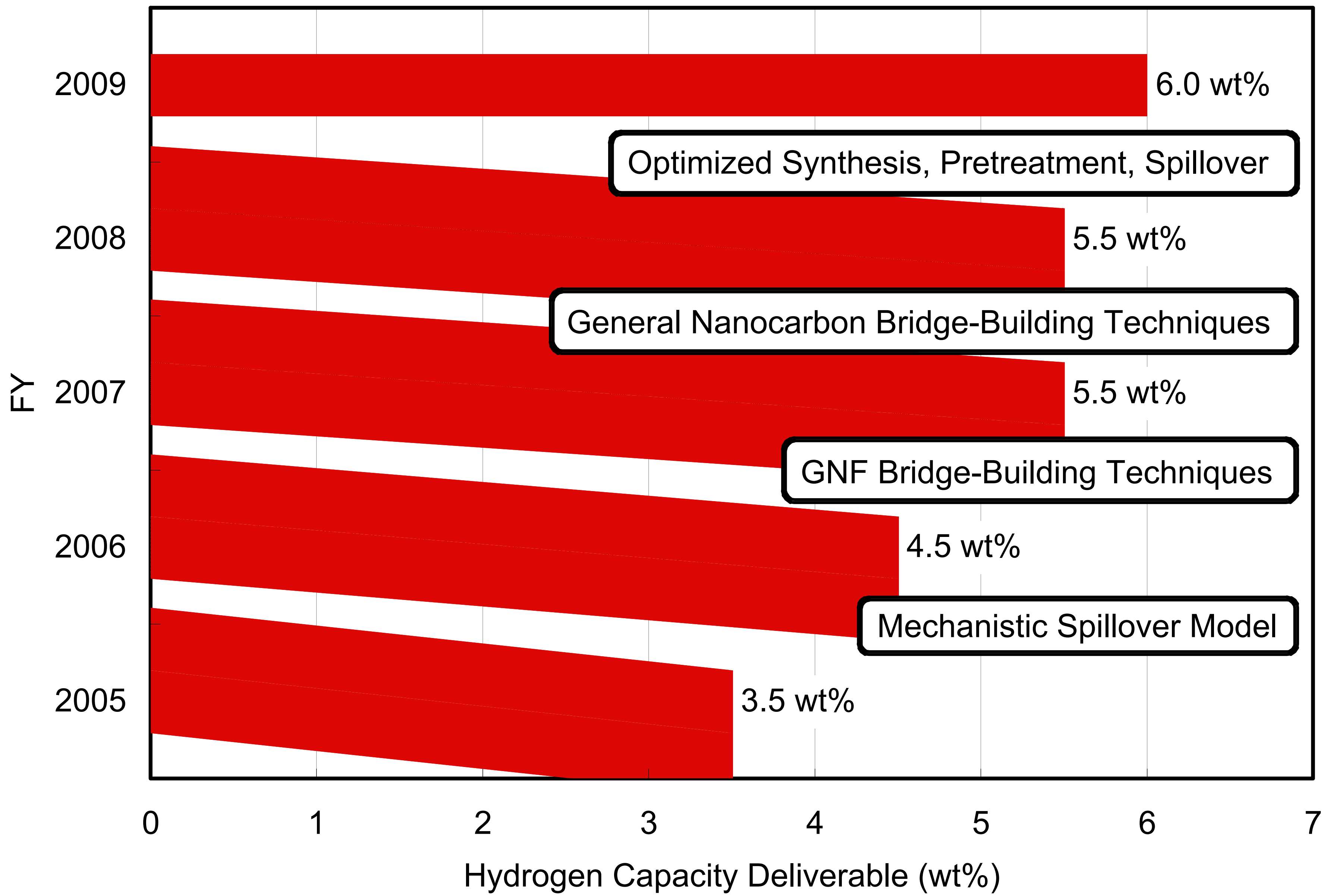
Project Milestones



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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

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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

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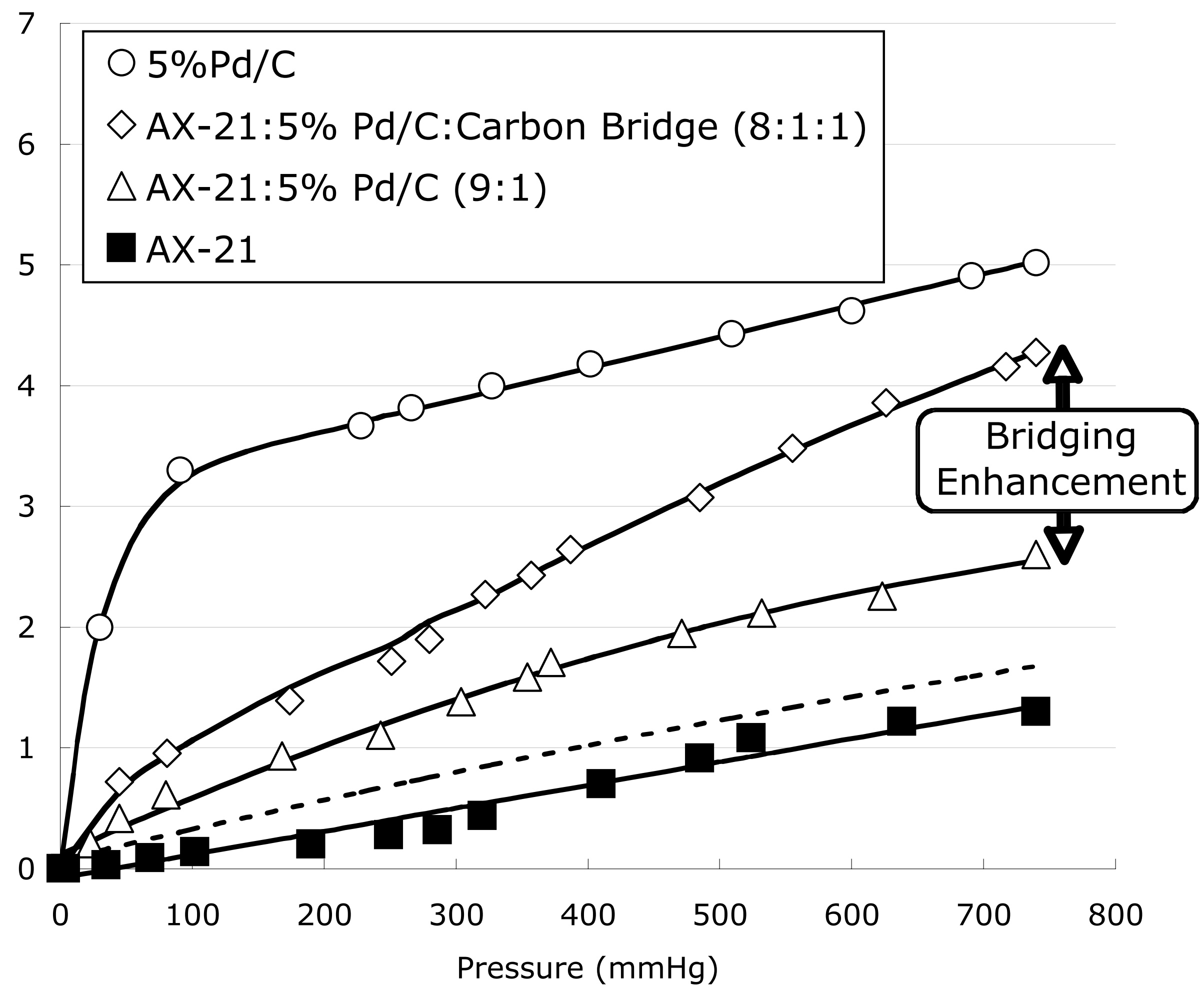
Low Pressure Spillover Enhancement

- 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)



Source: AX-21 Bridge Data: Unpublished Work, Lachawiec, Qi & Yang (2005)

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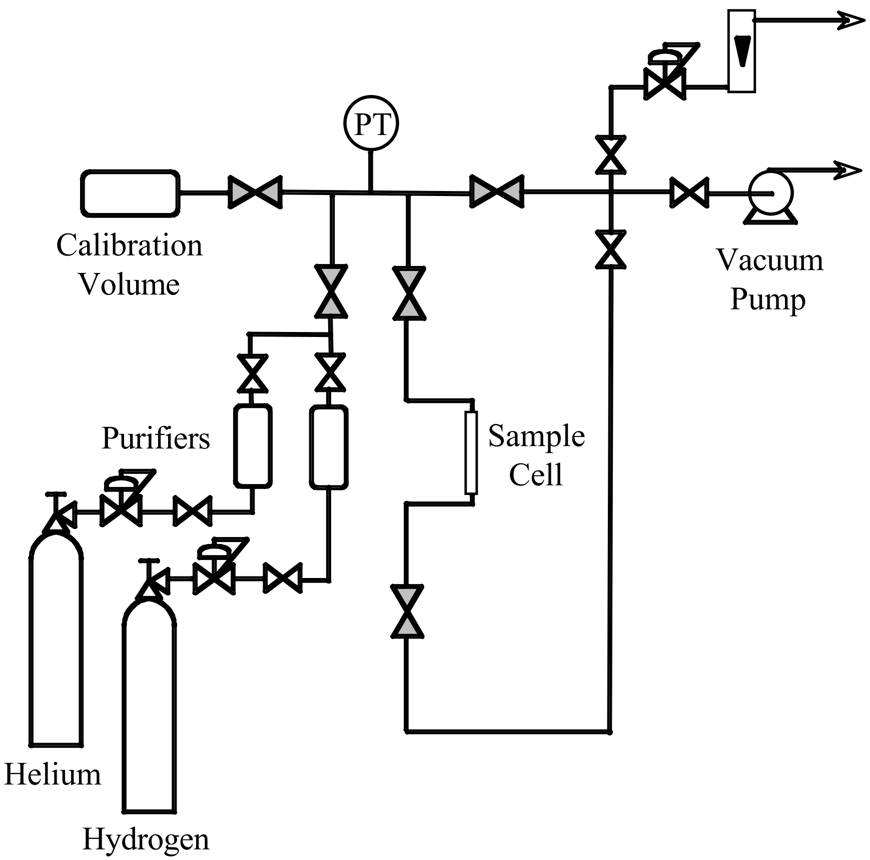
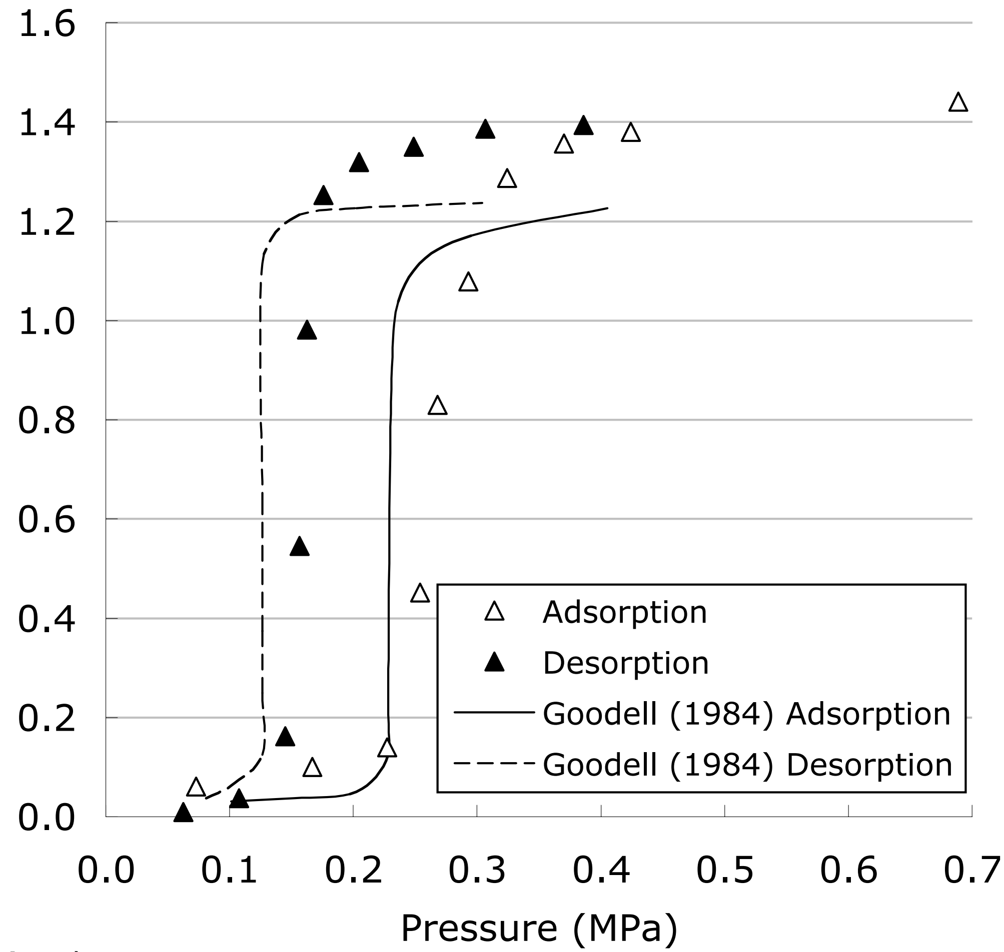
High Pressure Measurement



LaNi$_5$ Calibration



- 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)

Source: Goodell (1984) *J. Less-Common Met.* 99, 1

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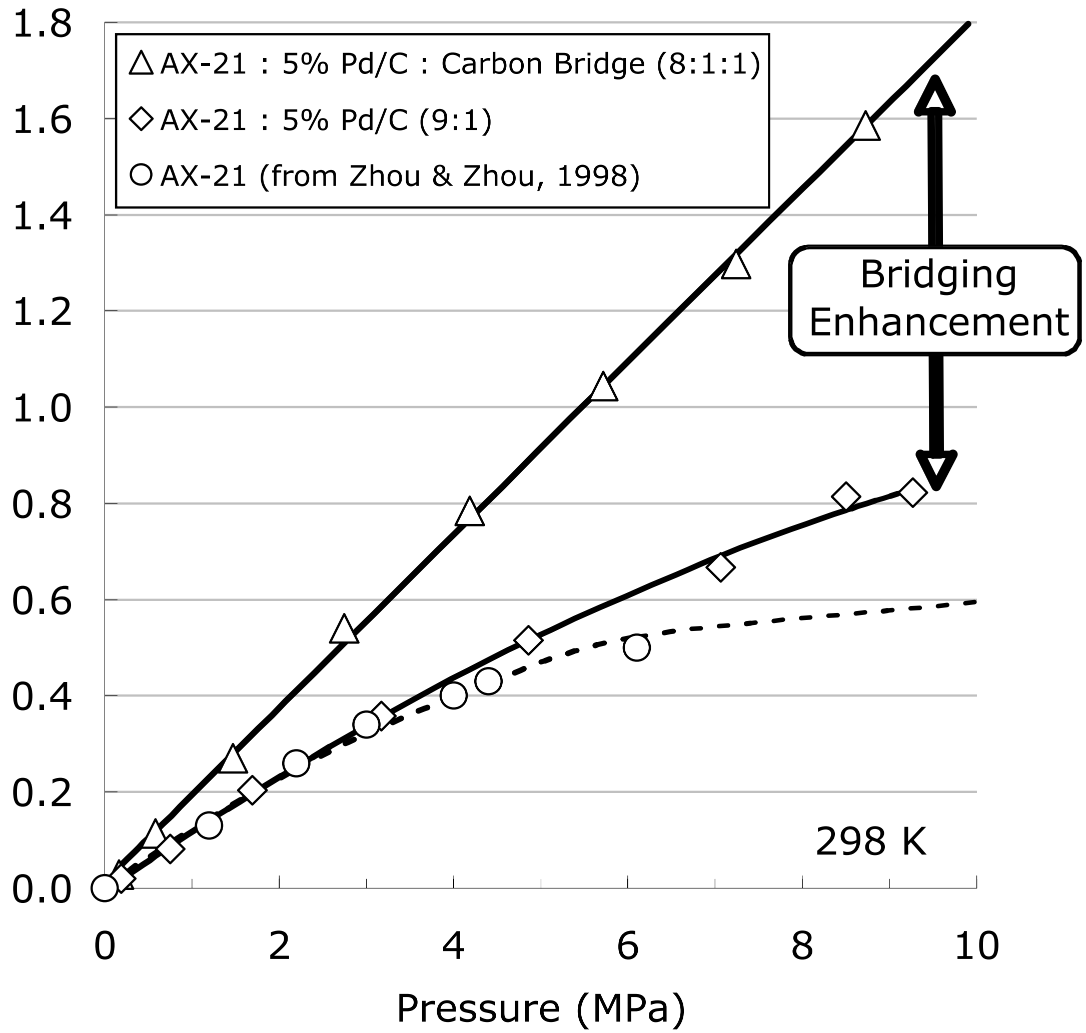
High Pressure Spillover Enhancement

- 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



Sources: AX-21 Bridge Data: Unpublished Work, Lachawiec, Qi & Yang (2005)
AX-21 Isotherm: Zhou & Zhou (1998) *Chem. Eng. Sci.* 53, 2531

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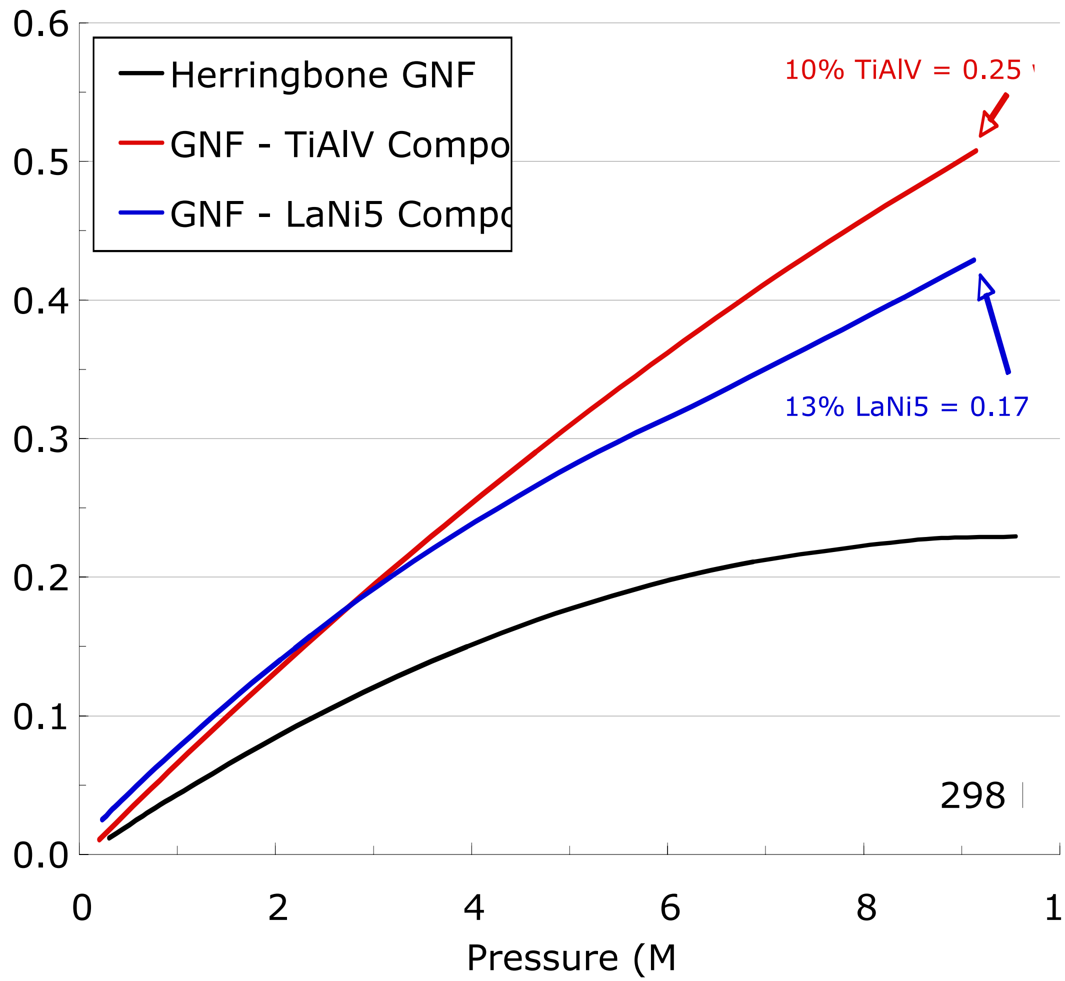
Graphite Nanofiber-Metal Hydride Composites

- 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



Source: Unpublished Work, Lachawiec and Yang (2005)

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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)

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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