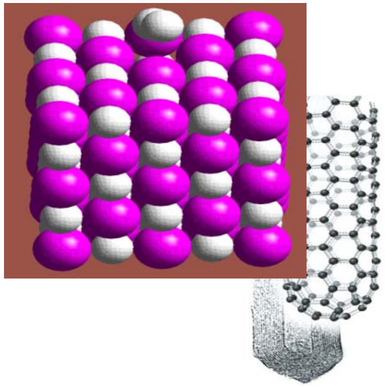
Standardized Testing Program for Solid-State Hydrogen Storage Technologies

Michael A. Miller
Institute Scientist

Richard Page
Institute Scientist

Southwest Research Institute®
National Testing Laboratory for Solid-State Hydrogen Storage Technologies
San Antonio, TX



DOE Annual Merit Review, Washington DC
May 9-13, 2011

This presentation does not contain any proprietary or confidential information

Project ST054

Overview

Timeline

Phase I

- Program Start: March 2002
- Program End: September 2006
- 100% Complete

Phase II

- Program Start: October 2006
- Program End: March 2012
- 85% Complete

Barriers

- Standardization of Methods
- "Gold Standard" Measurements
- Verification of Material Performance
  - (P) Understanding of Physisorption & Chemisorption Processes
  - (Q) Reproducibility of Performance
- Verification of System Performance
  - (Q) Reproducibility of Performance
  - (K) System Life-Cycle Assessment
- Codes & Standards (F)

Budget

Phase I

- DOE Share: $2.386M
- SwRI Share: $0.62M

Phase II

- DOE Share: $2.0M
- Funding Received in FY10: $216k
- Funding Planned in FY11: $200k

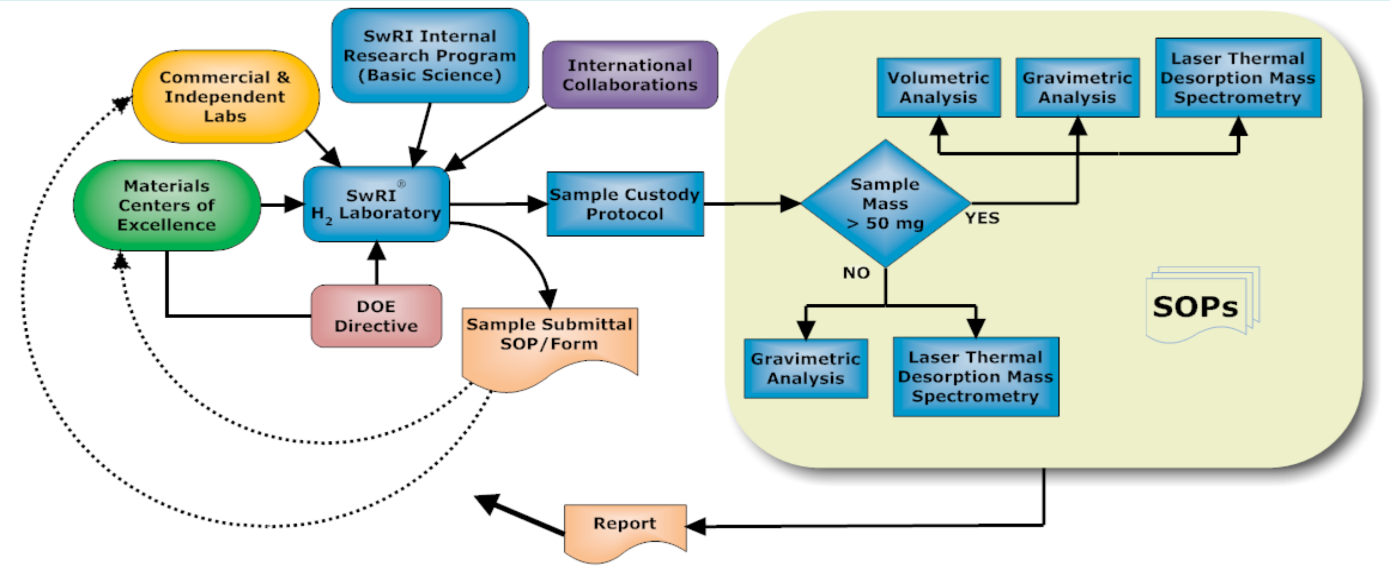
Partners / Collaborations

- INER (Taiwan)
- NESSHY (EC-JRC)
- Washington State University
- U. Idaho
- GoNano Technologies, Inc.

Objectives - Relevance

Overall

- Support DOE's Hydrogen Storage Program by operating an independent national-level laboratory aimed at assessing and validating the performance of novel and emerging solid-state hydrogen storage materials and full-scale systems
- Conduct measurements using established protocols to derive performance metrics: capacity, kinetics, thermodynamics, and cycle life
- Support parallel efforts underway within the international community, in Europe and Japan, to assess and validate the performance of related solid-state materials for hydrogen storage
- Validate the technologies required to achieve the 2015 DOE on-board vehicle hydrogen storage goals
- Continue new hydrogen storage materials discovery R&D for advanced storage systems



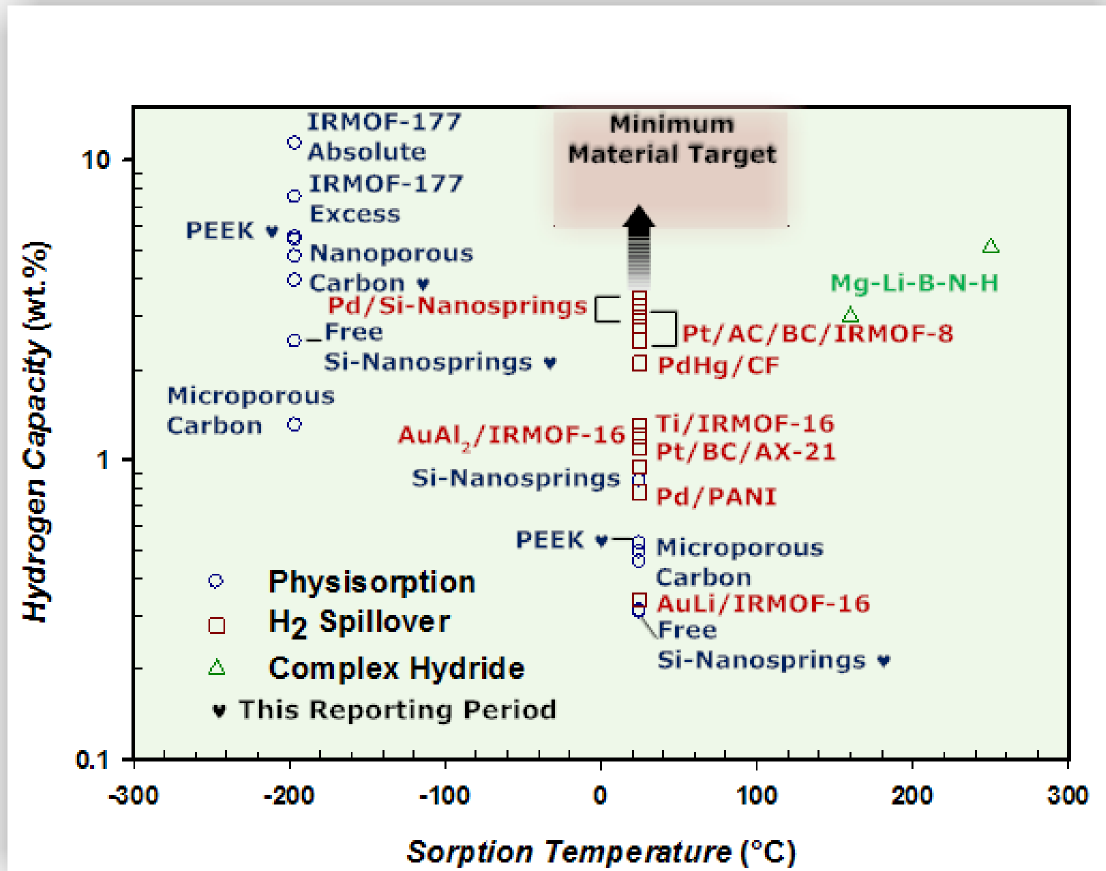
Objectives - Relevance

Current

Analyze hydrogen sorption properties at 77 and 298 K of:

- CO_2-activated PEEK-derived carbon
  (material provided by Duke Univ.)
- PEEK-derived carbon
  (material provided by SUNY)
- Microporous carbon
  (material provided by NREL)
- Glass nanosprings
  (material provided by GoNano™)
- Porous Polymer Network (PPN) ⇒ analysis underway
  (material provided by TAMU)

Status of Material Technologies for Reversible Hydrogen Storage via Physisorption, Spillover, and Chemisorption – In Proximity to DOE Target



Approach

DOE Directives

Receive physisorption materials
(Duke, NREL, SUNY, TAMU)

↓

Determine the skeletal density of each material using high-pressure gravimetric analysis at 298 K by treating it as a fitting parameter: simplified local density (SLD) model + Bender equation of state

↓

Determine the Gibbs excess-capacity of materials using high-pressure volumetric and gravimetric analyses at 77 and 298 K, respectively

↓

Derive the hydrogen-accessible pore volume of material from the SLD model

↓

Estimate the absolute volumetric capacity of materials at 77 K from the hydrogen-accessible pore volume and Gibbs excess

Internal / External Research

Synthesize Si-nanosprings on Al support
(GoNano, UI, WSU, SwRI collaboration)

↓

Chemically strip Si-nanosprings from Al substrate to produce free, unbound nanosprings

↓

Determine the skeletal density of free Si-nanosprings using high-pressure gravimetric analysis at 298 K by treating it as a fitting parameter: SLD model + Bender equation of state

↓

Evaluate the sorption properties of free Si-nanosprings using high-pressure volumetric and gravimetric analyses at 77 and 298 K, respectively

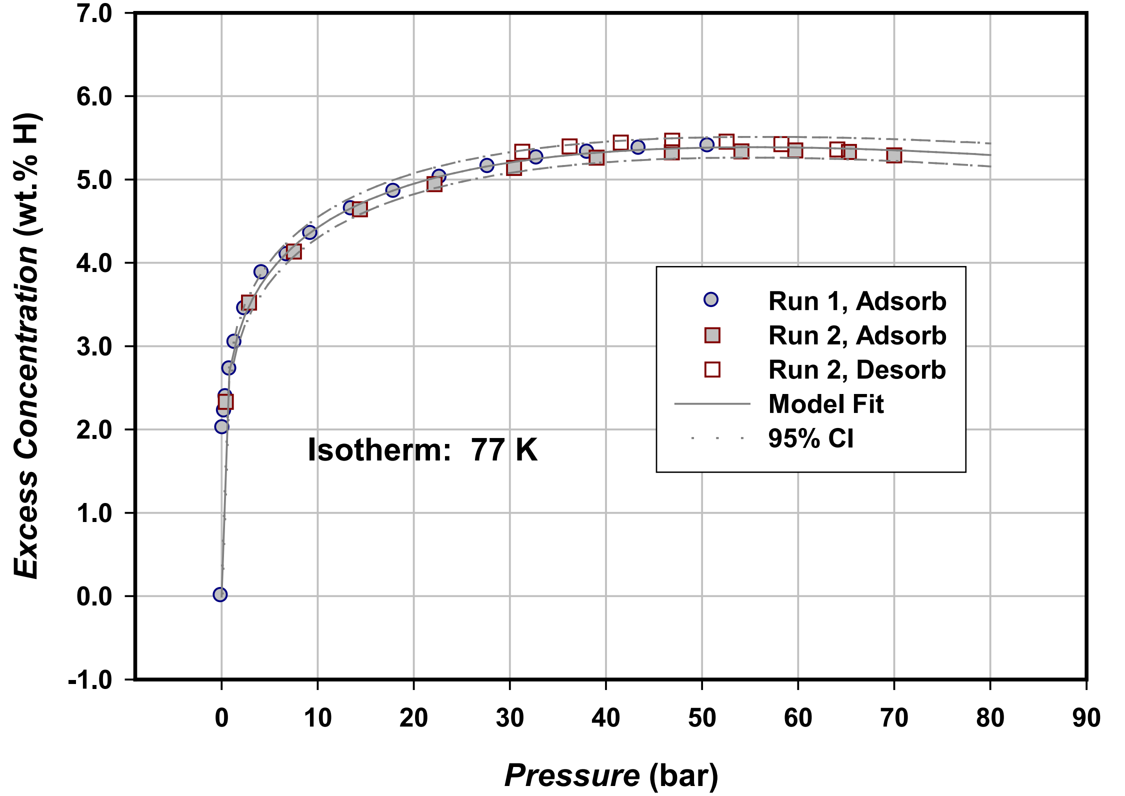
ACCOMPLISHMENTS IN RESPONSE TO DOE PRIORITIES & DIRECTIVES

Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in CO_2-Activated PEEK-Derived Carbon (Material Provided by Duke Univ.)

- Isotherm curves were corrected for the free volume of the sample (or skeletal density), as determined by gravimetric analysis
- Kinetics are relatively fast, reaching steady-state conditions within ~ 20 min
- Peak uptake of 5.39 wt.% at 55 bar
- No evidence of hysteresis
- Further verification and accuracy check of skeletal volume (and density) was done at 298 K via gravimetric analysis
- Pore volume derived from gravimetric analysis was used to estimate volumetric capacity

Corrected Hydrogen Isotherms at 77 K (Volumetric Analysis)



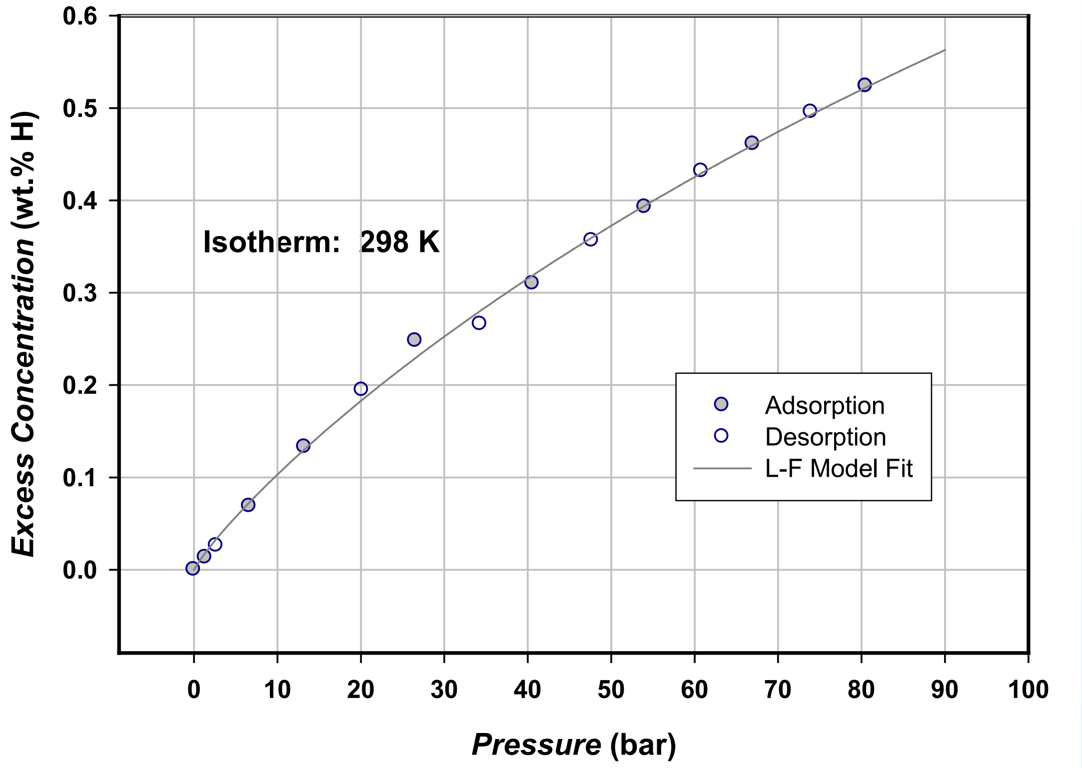
Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in CO_2-Activated PEEK-Derived Carbon (Material Provided by Duke Univ.)

- Isotherm at 298 K (gravimetric technique) was used to cross-check skeletal density and to semi-empirically predict pore volume
- Peak uptake of 0.52 wt.% at 80 bar
- Simplified Local Density (SLD) model combined with Bender Equation of State (BEOS) were employed to estimate pore volume

H_2-Derived Skeletal Density (g/cc)
3.92

Hydrogen Isotherm at 298 K (Gravimetric Analysis)



SLD Model for Gravimetric Gibbs Excess

$$W_a - W_{sb}\left(1-\frac{\rho_g}{\rho_{sb}}\right) - W_s\left(1-\frac{\rho_g}{\rho_s}\right) = V_{ad}\left(\rho_{ad}-\rho_g\right) \equiv \Gamma$$

Gibbs Excess

W_a = Apparent weight
W_{sb} = Weight of sample basket
W_s = Sample weight
ρ_g = Bulk-gas density
V_{ad} = Volume of adsorbed layer

Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in CO_2-Activated PEEK-Derived Carbon (Material Provided by Duke Univ.)

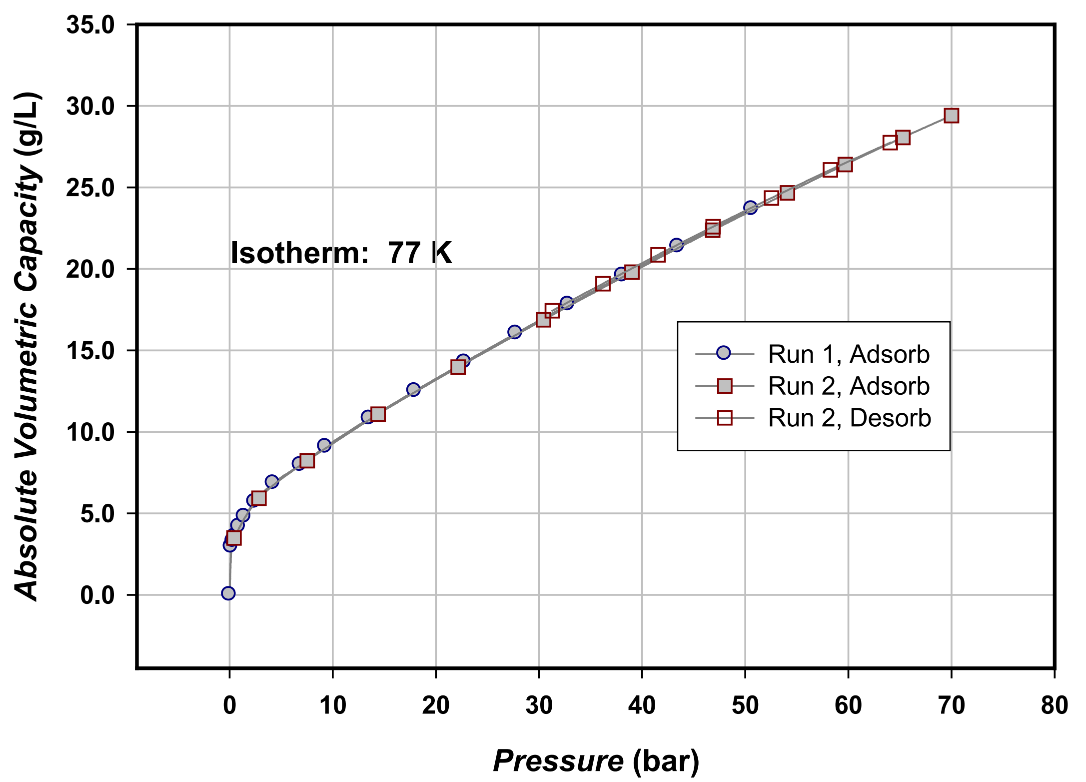
- Absolute volumetric capacity at 77 K approaches 30 g/L at 70 bar
- Absolute capacity estimated by:

$$n_{abs} = n_{ex} + \rho_{bulk} V_{pore}$$

- n_{abs} not directly accessible by experiment (semi-empirically determined from gravimetric measurement and SLD model)
- ρ_{bulk} determined from BEOS

H_2-Derived Specific Pore Volume (cc/g)	Total Pore Volume (cc)
6.62	13.16

Absolute Volumetric Capacity at 77 K (Volumetric Analysis)

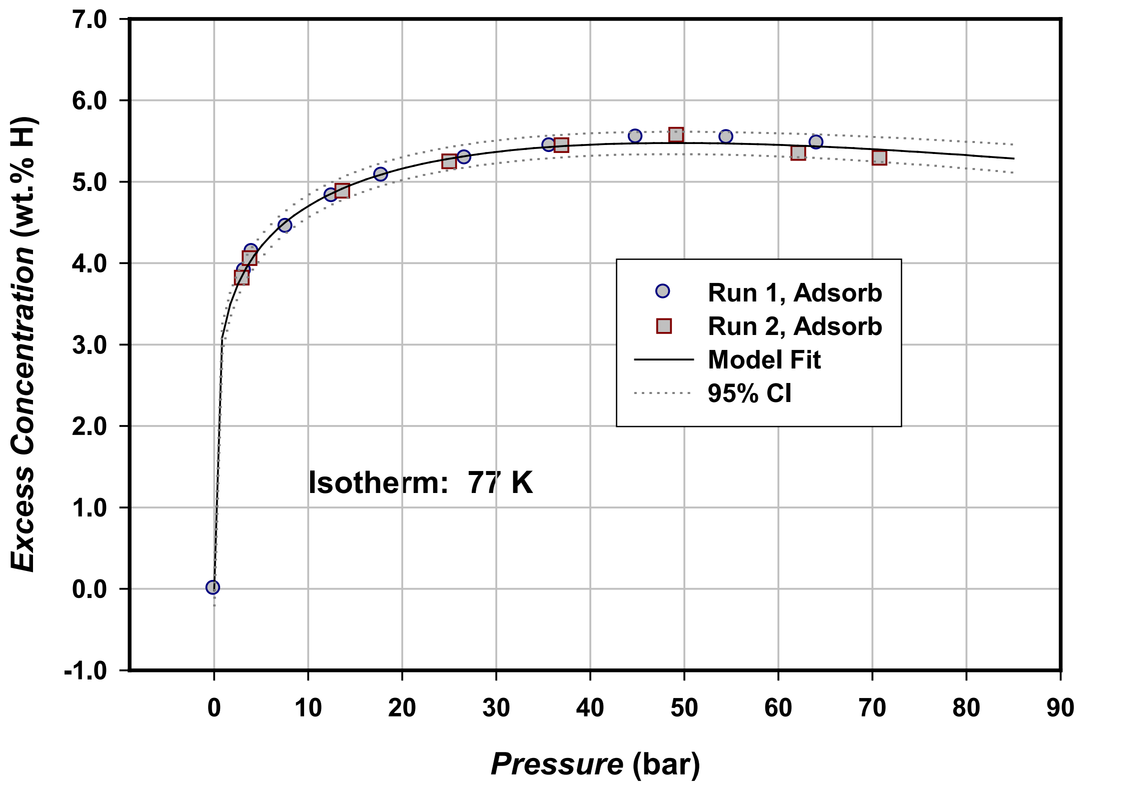


Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in PEEK-Derived Carbon (Material Provided by SUNY)

- Helium has measurable uptake in this material, leading to erroneous measurement of the skeletal density
- Hydrogen isotherms measured at 298 K via the gravimetric technique and SLD model were used to accurately determine skeletal density
- Isotherm curves at 77 K were corrected for the free volume of the sample (or skeletal density), as determined by gravimetric analysis
- Peak uptake of 5.50 wt.% at 49 bar

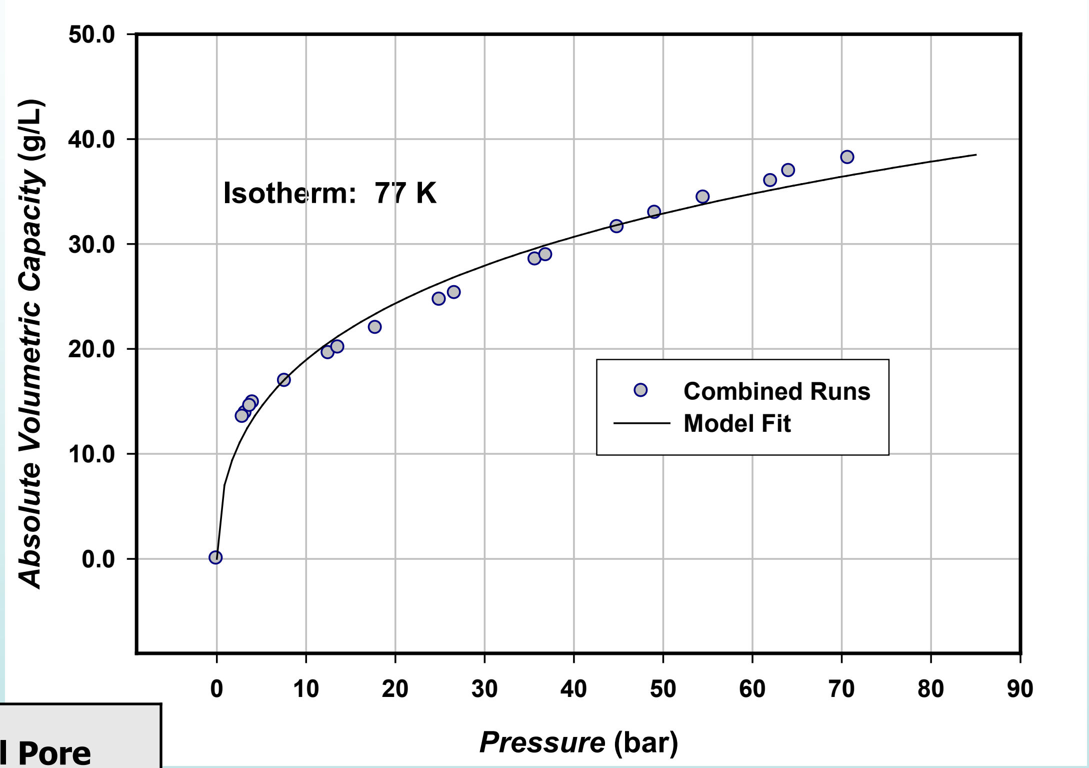
Corrected Hydrogen Isotherms at 77 K (Volumetric Analysis)



Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in PEEK-Derived Carbon (Material Provided by SUNY)

Absolute Volumetric Capacity at 77 K (Volumetric Analysis)



- Absolute volumetric capacity at 77 K approaches 38.2 g/L at 71 bar
- Pore volume derived from gravimetric analysis and SLD model was used to estimate volumetric capacity

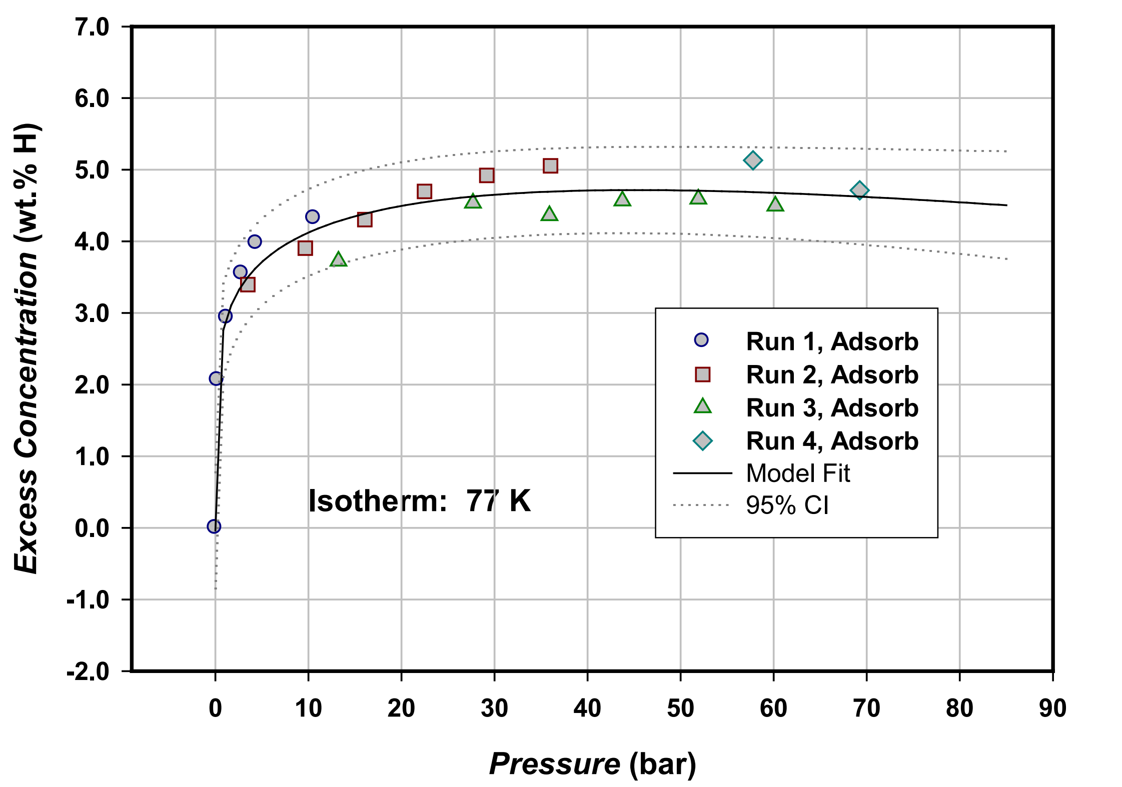
H_2-Derived Skeletal Density (g/cc)	H_2-Derived Specific Pore Volume (cc/g)	Total Pore Volume (cc)
3.70	2.69	2.32

Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in Microporous Carbon (Material Provided by NREL)

- Four analysis runs were required to build a complete isotherm curve due to slow kinetics (*i.e.*, long equilibration times)
- Material was thermally conditioned *in vacuo* after each adsorption cycle
- Peak uptake of 4.75 wt.% at 45 bar
- Larger than normal scatter in isotherm curve is due to thermal conditioning between analysis runs

Absolute Volumetric Capacity at 77 K (Volumetric Analysis)



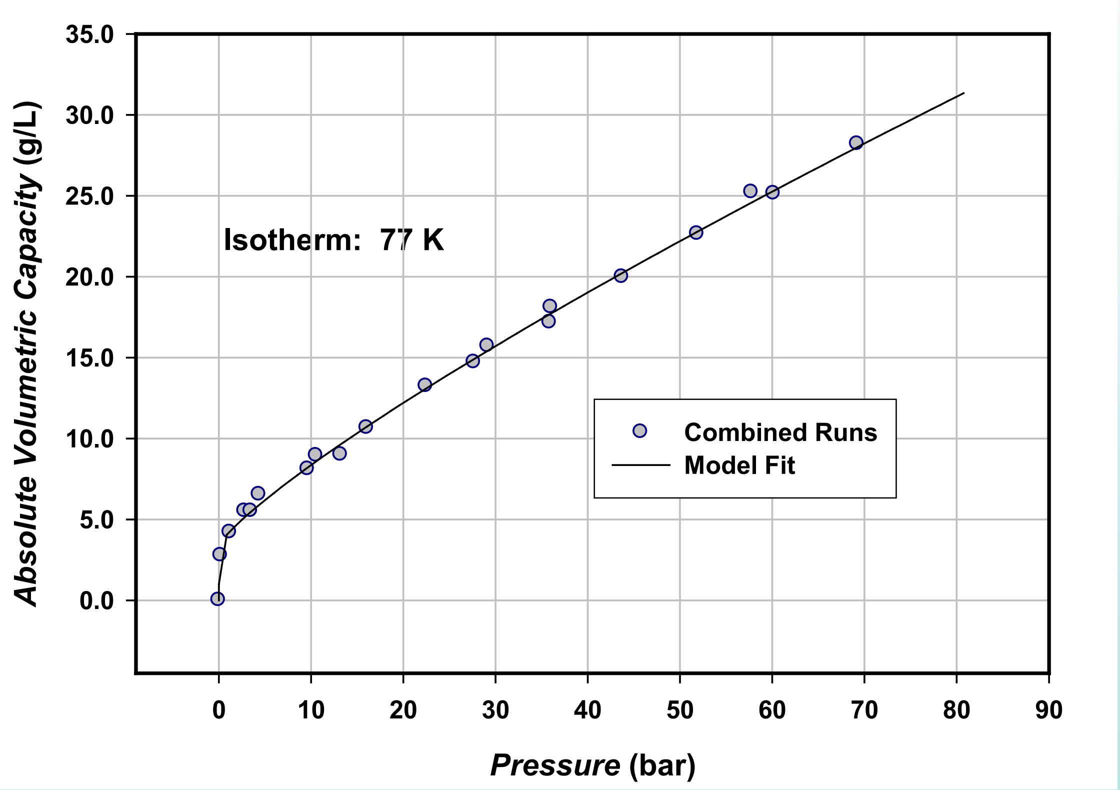
Accomplishments – DOE Directives

Evaluate/Validate Hydrogen Sorption in Microporous Carbon (Material Provided by NREL)

- Absolute volumetric capacity at 77 K approaches 28.2 g/L at 70 bar
- Pore volume derived from gravimetric analysis and SLD model was used to estimate volumetric capacity

H_2-Derived Skeletal Density (g/cc)	Total Pore Volume (cc)
4.90	1.74

Corrected Hydrogen Isotherms at 77 K (Volumetric Analysis)

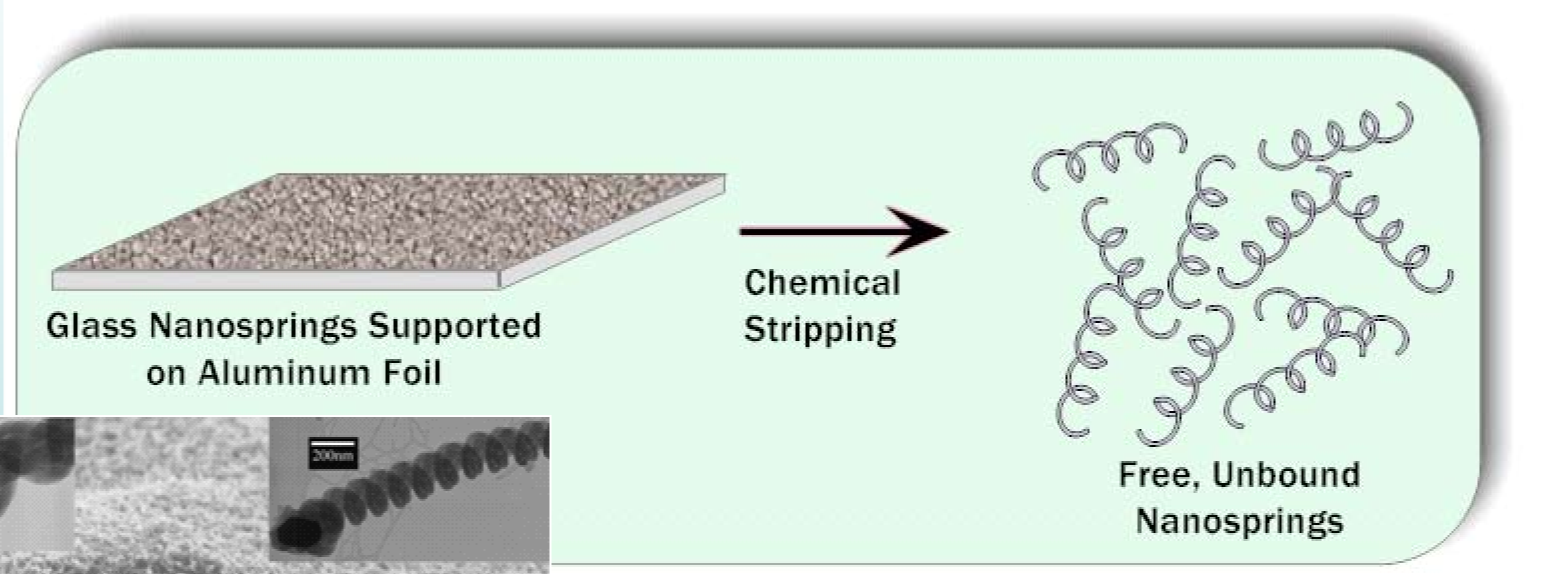


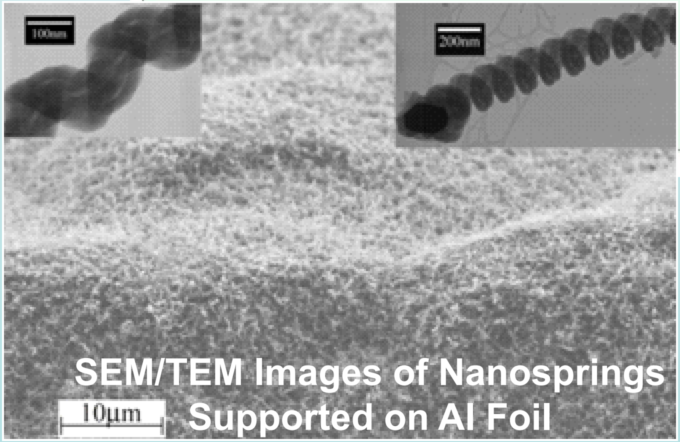
ACCOMPLISHMENTS RELATED TO SWRI'S INTERNAL & EXTERNAL RESEARCH COLLABORATIONS

Accomplishments – External Collaboration

Hydrogen Uptake in Free Silica Nanosprings

Motivation: Silica nanosprings consist of braided nanowires, forming continuous nano-scale troughs between wires that serve as interstitial sites for physisorption. This work is aimed at gaining a better understanding of the hydrogen sorption behavior of these novel materials by circumventing the analytical challenges previously encountered with measuring hydrogen sorption in Al-supported nanosprings.





SEM/TEM Images of Nanosprings Supported on Al Foil

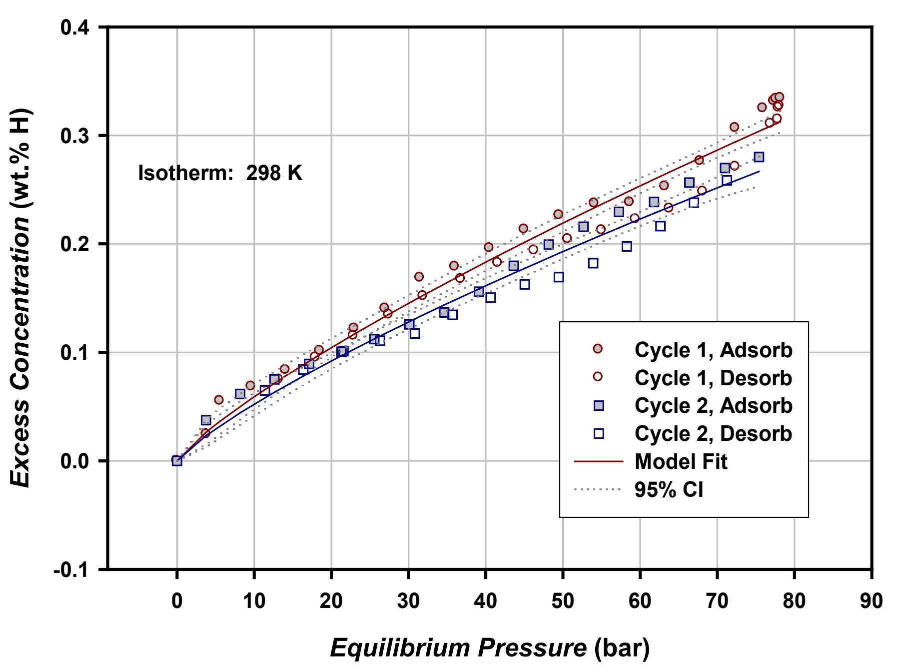
Free, unbound nanosprings require careful analytical practices and material handling in order to accurately measure hydrogen sorption, due to their low bulk density and propensity to fluidize at elevated gas pressures.

Accomplishments – External Collaboration

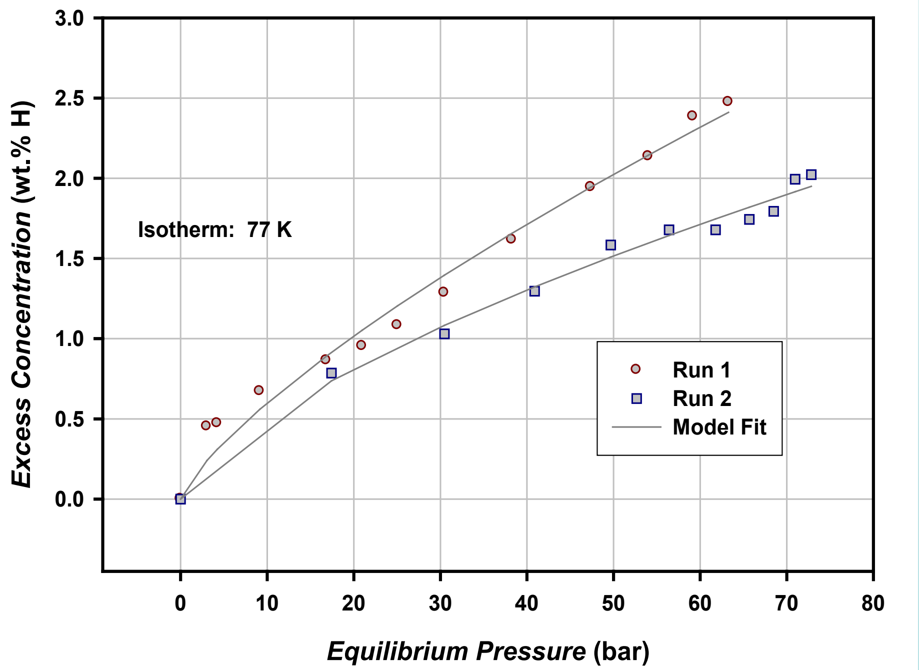
Hydrogen Uptake in Free Silica Nanosprings

- Preparation of free, unbound nanosprings (*i.e.*, not anchored to Al substrate) permits more accurate analysis of hydrogen uptake than has been previously possible with their Al-supported counterparts
- Peak uptake ranges 0.27 – 0.31 wt.% at 298 K and 75 bar, and 1.75 – 2.47 wt.% at 77 K and 63 bar
- Adsorption profiles exhibit measureable irreversibility following additional cycles or complete runs with thermal reconditioning, which is consistent with previous measurements for Al-supported nanosprings
- Maximum Gibbs excess not observed at 77 K up to 75 bar

Hydrogen Isotherm at 298 K (Volumetric Analysis)



Hydrogen Isotherm at 77 K (Volumetric Analysis)



Future Work (FY11)

Completed
Underway

Sample No.	Organization / Collaborator	Sample Type	Analysis	Date Received	Scheduled Start Date	Estimated Completion Date	Priority	Comments
1	WSU/GoNano Tech.	Pd-Doped Silica Nanosprings	LTDMS / Volumetric, 295 K	9/17/2009	12/3/2009	1/15/2010	Med	Independent Collaboration
2	Duke	Carbon	Volumetric, 77 K	3/25/2010	4/5/2010	4/23/2010	High	DOE Directive
3	NREL	Carbon	Volumetric, 77 K	4/5/2010	4/26/2010	4/30/2010	High	DOE Directive
4	SUNY	Carbon	Volumetric, 77 K	6/22/2010	7/5/2010	7/24/2010	High	DOE Directive
5	TAMU	MOF	Volumetric, 77 K	8/18/2010	10/11/2010	12/6/2010	High	DOE Directive
6	WSU/GoNano Tech.	TiO2-Doped Silica Nanosprings	LTDMS / Grav. / Vol., 295 K	9/17/2009	2/15/2010	5/7/2010	Med	Independent Collaboration
7	WSU/GoNano Tech.	Free Silica Nanosprings	Volumetric, 298 and 77 K	8/27/2010	1/18/2011	2/4/2011	Med	Independent Collaboration
8	NREL	Carbon, Round-Robin Interlaboratory Validation	Gravimetric, 298 K Volumetric, 298 and 77 K	11/16/2010	1/10/2011	4/08/2011	High	DOE Directive
9	TAMU	Porous Polymer	Volumetric, 298 and 77 K	NA	2/14/2011	3/25/2011	High	DOE Directive
10	WSU/GoNano Tech.	Pd-Doped Free Silica Nanosprings	Volumetric / Grav. 298 K	NA	3/21/2011	4/22/2011	Med	Independent Collaboration

Summary

Material	Material Provided by	Surface Excess Amount (wt.% H)		Absolute Volumetric Capacity (g/L) 77 K	MOF-177 Benchmark 77 K	
		298 K	77 K		(wt.% H)	(g/L)
CO_2-Activated PEEK-Derived Carbon	Duke University	0.52 @ 80 bar	5.39 @ 55 bar	30 @ 70 bar	7.5 @ 70 bar	47 @ 70 bar
PEEK-Derived Carbon	SUNY	0.31 @ 81 bar	5.50 @ 49 bar	38 @ 71 bar		
Microporous Carbon	NREL	0.49 @ 80 bar	4.75 @ 45 bar	28 @ 70 bar		
Free Glass Nanosprings	GoNano, Inc.	0.27-0.31 @ 75 bar	1.75-2.47 @ 63 bar	ND		