Standardized Testing Program for Solid-State Hydrogen Storage Technologies

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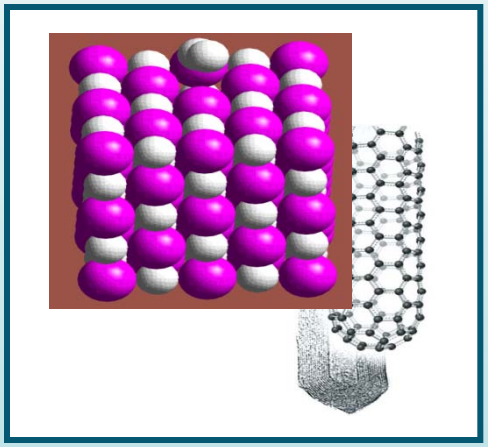


DOE Annual Merit Review, Washington DC
June 7-11, 2010

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: September 2011
- 80% 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: $2.475M
- SwRI Share: $0.62M

Phase II

- DOE Share: $2.0M
- Funding Received in FY09: $375k
- Funding Received in FY10: $142k

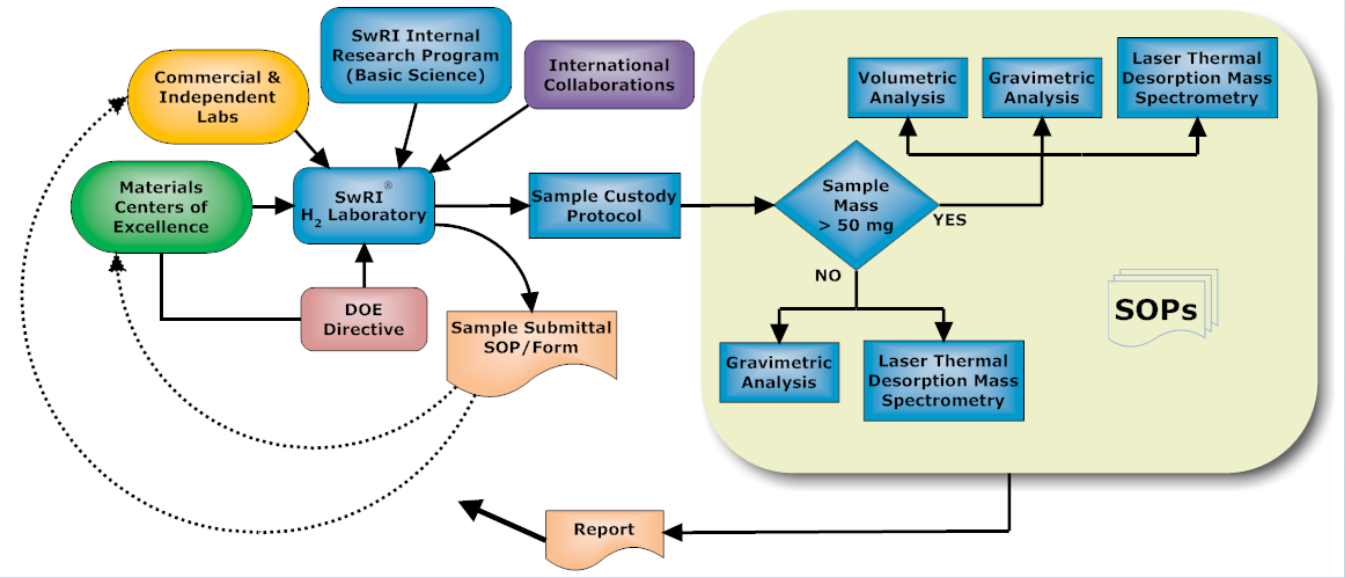
Partners / Collaborations

- 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

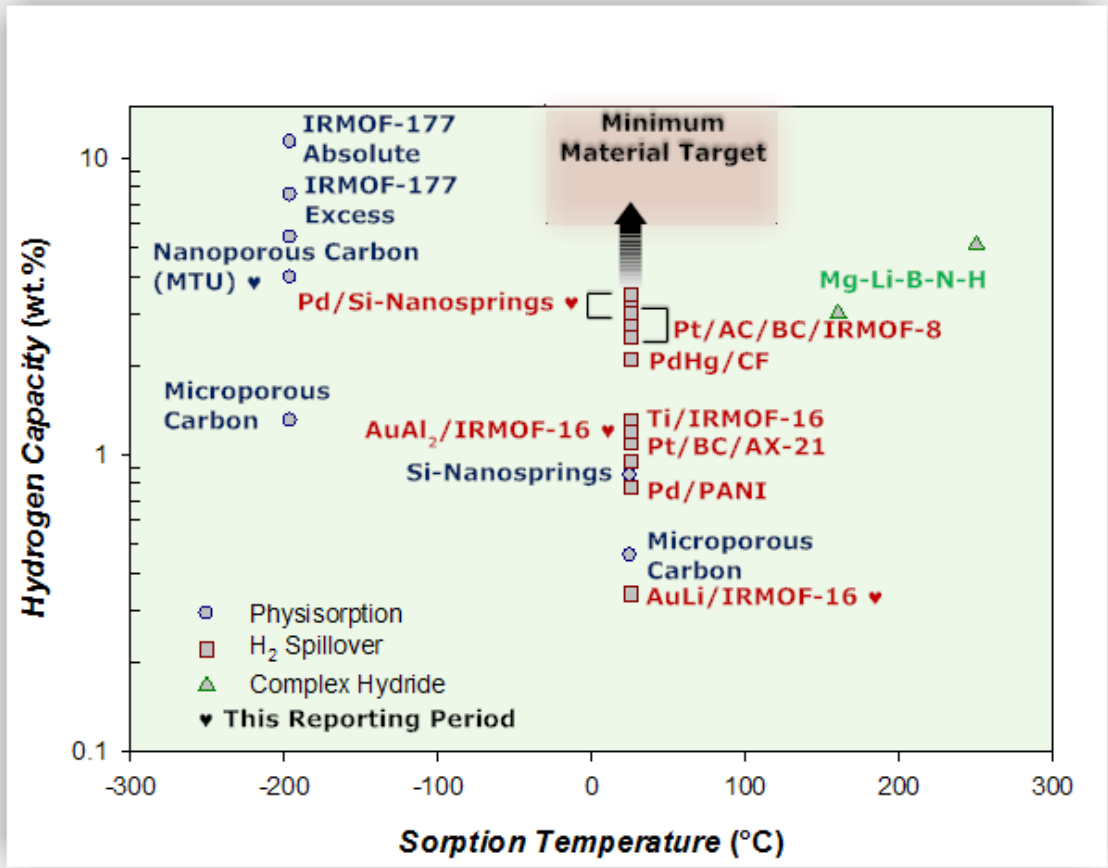


Objectives - Relevance

Current

- Evaluate/validate the effects of piezo-induced charge on the sorption capacity of nanoporous carbon
- Assess hydrogen spillover effects and kinetics in $AuAl_2$ – intercalated IRMOF-16
- Assess hydrogen spillover and kinetics in AuLi – intercalated IRMOF-16
- Assess hydrogen spillover and kinetics in Pd-doped silica nanosprings
- Continue Round-Robin testing in collaboration with the EU's hydrogen storage program (NESSHY)

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



Approach

DOE Directives

Assess effect of piezo-induced charge on hydrogen capacity of nanoporous carbon at 77 K (samples provided by MTU)

09/11/2009

Design and assemble special vessel with thin-walled glass insert

Determine skeletal density of nanoporous carbon sample using high-pressure gravimetric analysis at 298 K

Evaluate sorption capacity of nanoporous carbon sample at 77 K using high-pressure volumetric analysis, comparing the effects with and without PMN-PT piezoelectric elements embedded in sample

10/22/2009

EU (NESSHY) Collaboration

Round-Robin Testing of alanate sample in collaboration with the EU's NESSHY program

12/12/2008

Compile and compare inter-laboratory results

10/2009

Implement procedural changes in analytical methods if needed

Internal / External Research

Synthesize $AuAl_2$ and AuLi - intercalated IRMOF-16 for H_2 spillover (SwRI materials)

Evaluate sorption properties of metal-intercalated IRMOF-16 using high-pressure gravimetric analyses at 298 K

09/28/2009

Synthesize Pd-doped Si-nanosprings for H_2 spillover (GoNano, UI, WSU, SwRI collaboration)

Evaluate sorption Properties of Pd/Si-nanosprings using high-pressure volumetric analysis at 298 K

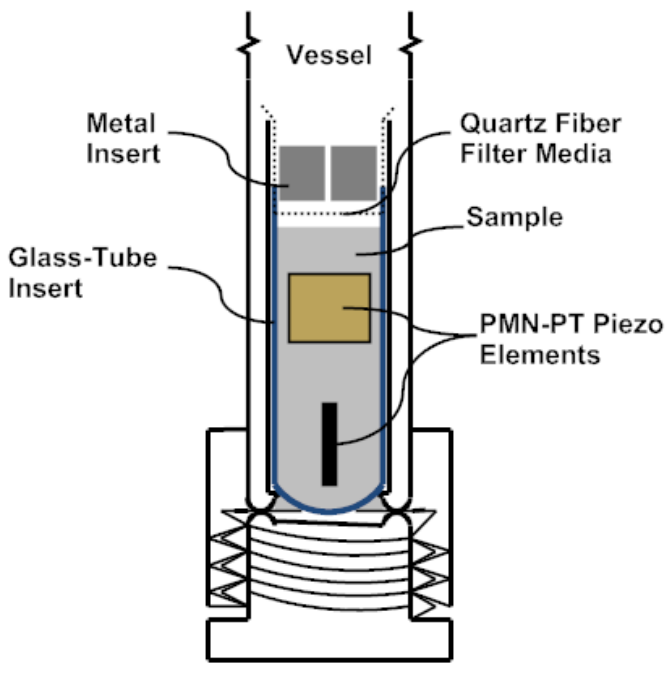
02/11/2010

ACCOMPLISHMENTS IN RESPONSE TO DOE PRIORITIES & DIRECTIVES

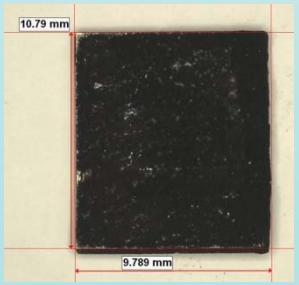
Accomplishments – DOE Directives

Evaluate/Validate Effect of Piezo-Induced Charge on Hydrogen Adsorption in Nanoporous Carbon (Materials Provided by Mich. Tech. Univ.)

- Embedded PMN-PT piezoelectric elements (~10×10 mm) in sample
- One pole (face) of piezo elements was electrically insulated with polymeric coating
- Carbon sample was electrically insulated from vessel – required design and assembly of specially-configured sample vessel
- Sample vessel was designed to minimize free volume ("dead" volume)
- Multiple sorption isotherms conducted at 77 K



$Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ (PMN–PT)



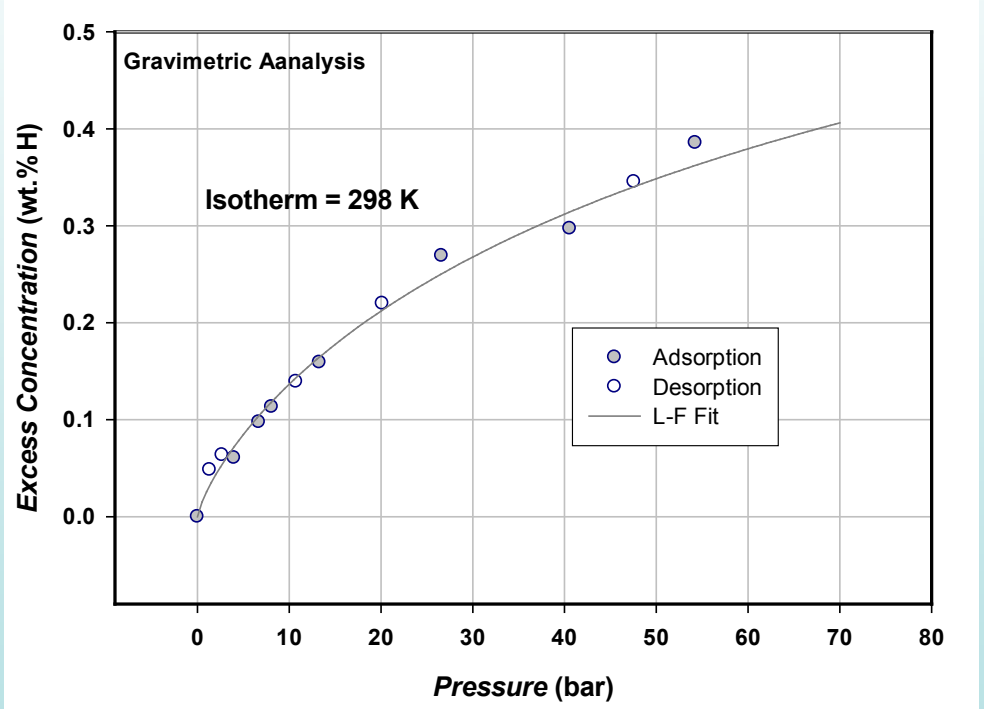
Piezo element after removal from sample vessel

Accomplishments – DOE Directives

Evaluate/Validate Effect of Piezo-Induced Charge on Hydrogen Adsorption in Nanoporous Carbon (Materials Provided by Mich. Tech. Univ.)

- Significant He adsorption necessitated independent measurement of sample skeletal density via gravimetric analysis at 298 K
- Three-parameter fitting procedure employing Bender equation of state (BEOS), fugacity, and chemical potential was used to derive sample skeletal density from hydrogen isotherm
- Maximum reversible uptake was 0.39 wt.% at 54 bar
- Semi-empirical determination of sample skeletal density used to properly calibrate free volume in high-pressure volumetric apparatus

Hydrogen Isotherm for Determining Skeletal Density

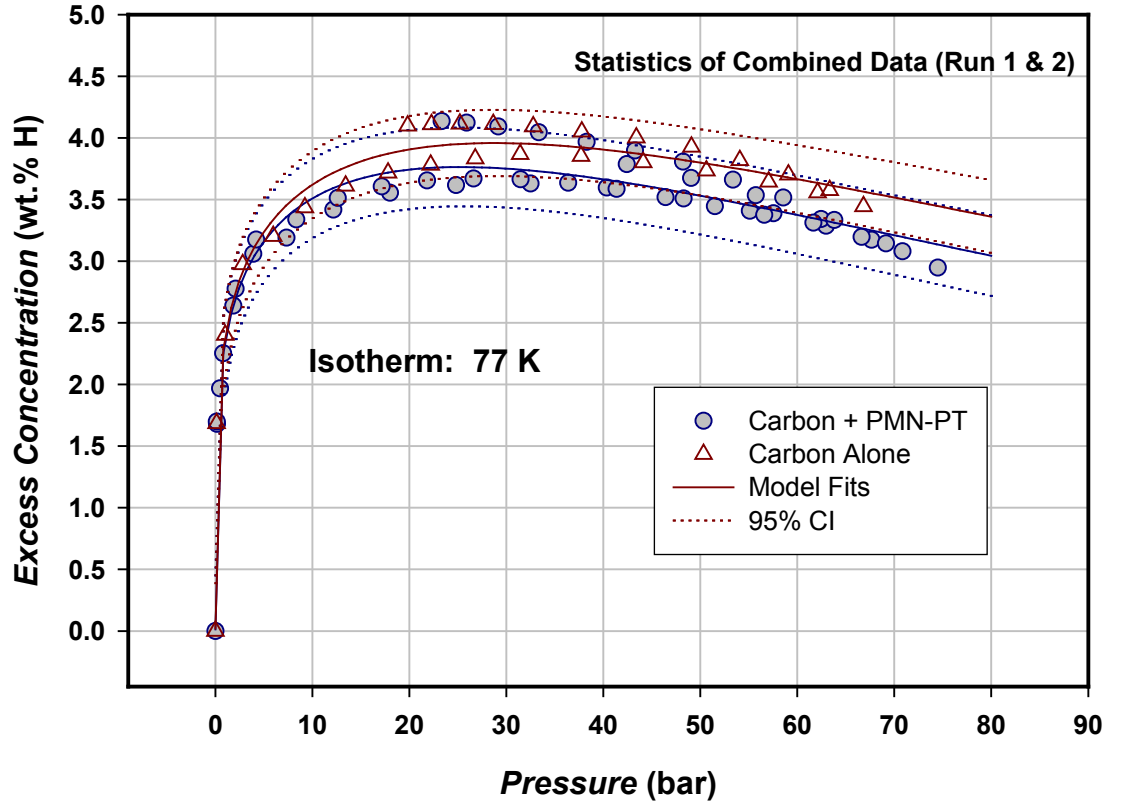


Accomplishments – DOE Directives

Evaluate/Validate Effect of Piezo-Induced Charge on Hydrogen Adsorption in Nanoporous Carbon (Materials Provided by Mich. Tech. Univ.)

- Isotherm curves properly corrected for the free volume of the sample (or skeletal density), as determined by gravimetric analysis, and the volume of the piezo elements
- Plot compares isotherm curves for carbon alone and carbon plus piezo elements, each measured identically at 77 K
- No experimentally significant difference in hydrogen uptake between the two cases
- Peak uptake of 3.94 wt.% at 29 bar for carbon alone, vs. 3.84 wt.% at 24 bar for carbon + PMN-PT elements

Corrected Hydrogen Isotherms at 77 K (Volumetric Analysis)

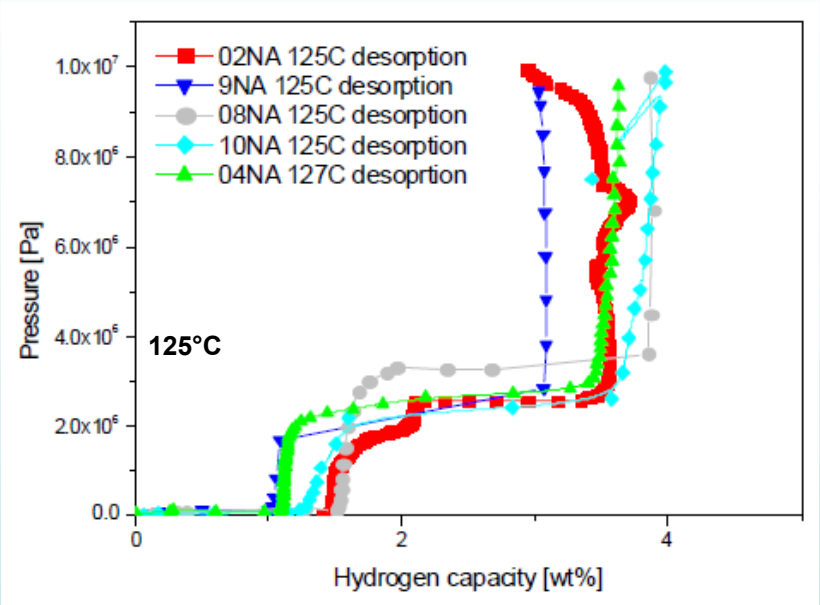


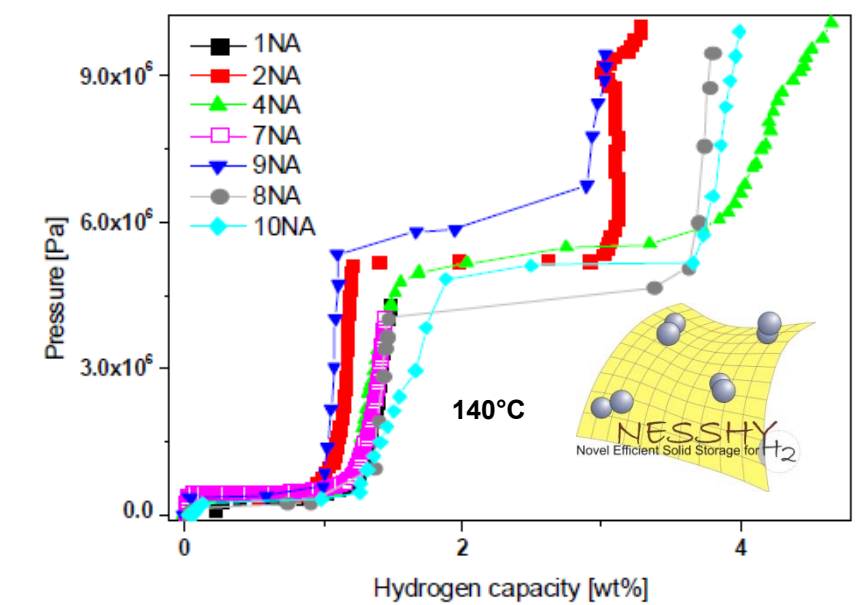
Results indicate that under the conditions in which SwRI performed these measurements, piezo-induced charge accumulation does not lead to a measureable increase in hydrogen uptake via hydrogen-charge binding interactions.

ACCOMPLISHMENTS RELATED TO EU (NESSHY) ACTIVITIES

Accomplishments – NESSHY Collaboration

NESSHY Round-Robin Testing Results for $NaAlH_4$ ($CeCl_3$ Catalyzed)





- A total of seven NESSHY partners participated in RRT, each one measured PCT isotherms (desorption and absorption) at two temperatures (125°C and 140°C) following the same preconditioning protocol
- Comparative results again show scatter in the measurements, though less scatter than the RRT study for physisorption in a carbon material at 77 K
- Overall, the results of this RRT study demonstrate the need to further develop standard guidelines for experimental procedures so that comparable and accurate quantitative results can be achieved among independent laboratories

ACCOMPLISHMENTS RELATED TO SWRI'S INTERNAL & EXTERNAL RESEARCH COLLABORATIONS

Accomplishments – Internal Research

Intercalation of Metallic Nanoparticles in IRMOF-16 for Enhanced Storage at Room Temperature via H_2 Spillover and Fast Kinetics: The $AuAl_2$ and AuLi Systems

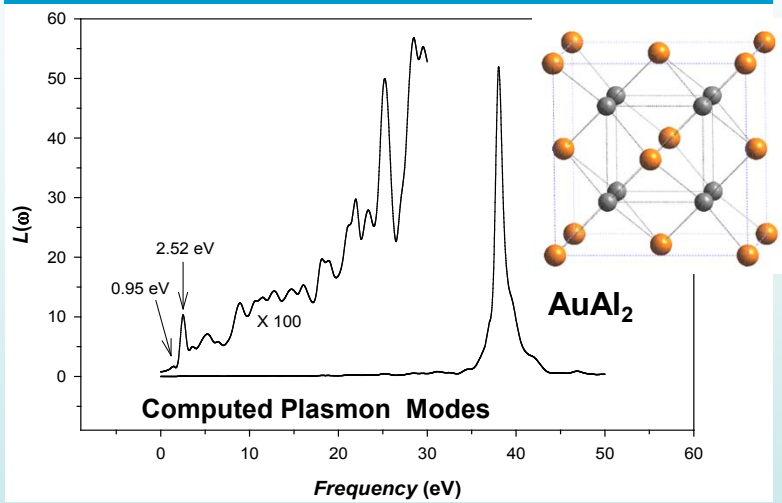
Goals:

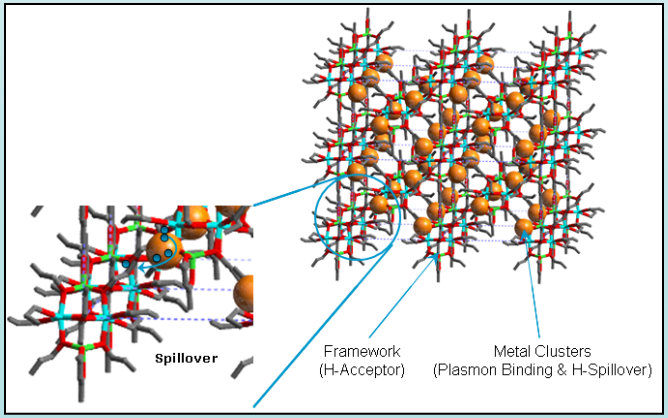
- Select alternative catalysts for intercalating IRMOF-16 and effecting hydrogen uptake via spillover with fast kinetics
- Compute density of states and plasmon modes available for vibrational coupling of H_2 in candidate pure metals and metal compounds using FP-LMTO level of theory
- Synthesize metal-intercalated IRMOF-16
- Measure hydrogen uptake and kinetics

Motivation: Porous materials exhibiting enhanced uptake at room temperature via hydrogen spillover have been consistently plagued by exceedingly slow kinetics, principally because doping of these materials with catalyst (and bridging compounds) has been limited to the surface

Strategy: Intercalate catalyst nanoparticles into the voids (or pores) of a porous receptor, such as MOF, thus reducing the diffusion length for spillover of atomic hydrogen

Full-Potential, Linear-Muffin-Tin-Orbital Theory (FP-LMTO)

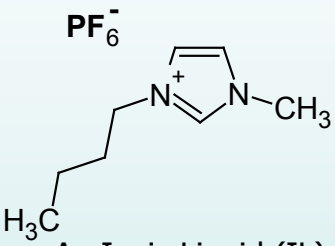




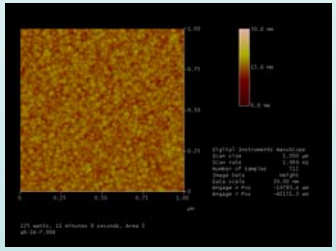
Accomplishments – Internal Research

Synthesis of Metal-Intercalated IRMOF-16 for Hydrogen Storage via Spillover

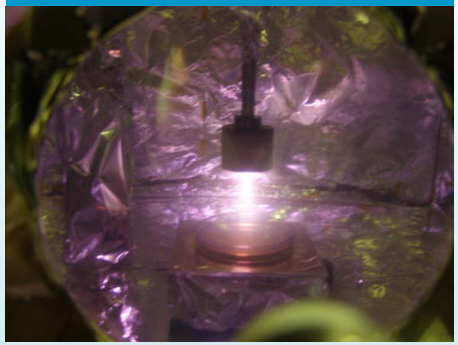
Step 1 – Synthesis of Free-Flowing Metal Clusters in IL



An Ionic Liquid (IL)



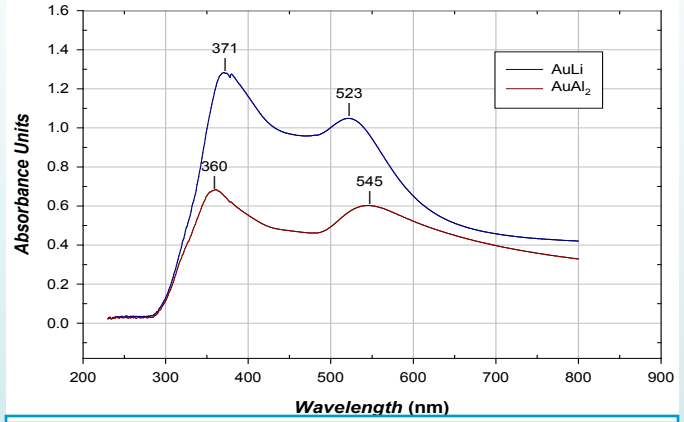
Plasma Magnetron Deposition into Liquid Pool (*in vacuo*)



AFM Results
Mean Diameter: 22.6 nm
Range: 2.20 – 161 nm

Non-Aggregating Metal Clusters in IL Pool

UV-VIS Absorption Spectra



Plasmon absorption peaks (due to quadrupole resonance) confirms synthesis of small clusters

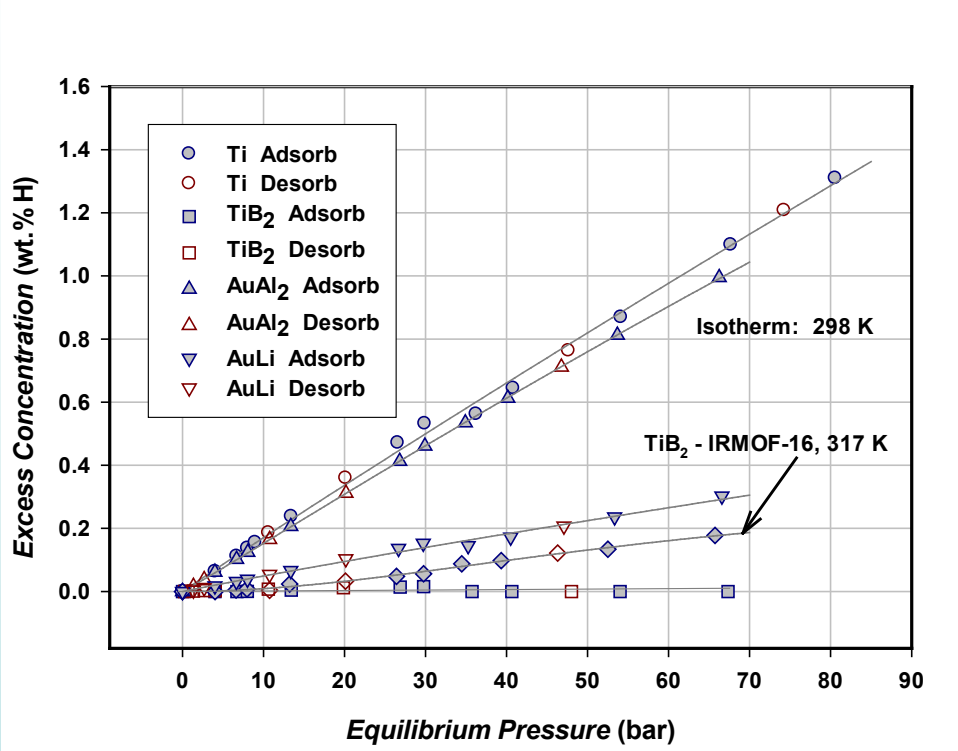
Step 2 – In Situ Intercalation of Metal Clusters into Framework

$$AuAl_2 \text{ or AuLi Clusters} + \text{1,4-di(4-carboxyphenyl)benzene} + Zn(NO_3)_2{\cdot}6H_2O \xrightarrow[\text{DEF}]{\text{IL}} \text{Metal-Intercalated IRMOF-16}$$

Accomplishments – Internal Research

Hydrogen Uptake in Metal Intercalated IRMOF-16

ICP-MS Metals Analyses	
Metal Compound	Amount Intercalated (wt. %)
Ti	0.0351
TiB_2	0.0549
$AuAl_2$	0.133
AuLi	0.0958



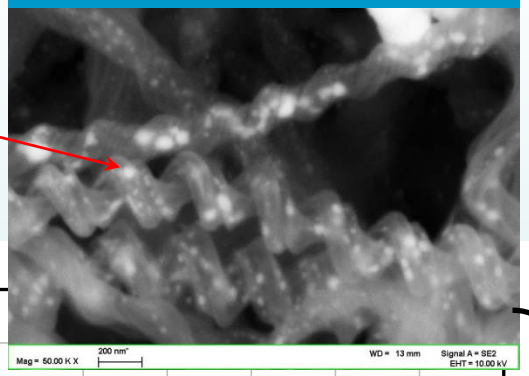
- Enhanced hydrogen uptake at room temperature via spillover is observed for $AuAl_2$-IRMOF-16, 1.1 wt.% at 80 bar (similar to Ti-IRMOF-16)
- Total catalyst loading (intercalated) is very low as determined by ICP-MS
- Fast spillover kinetics compared with other materials studied (~ 15 min vs. 600 min for Pt/AC/BC/IRMOF-8)

Accomplishments – External Collaboration

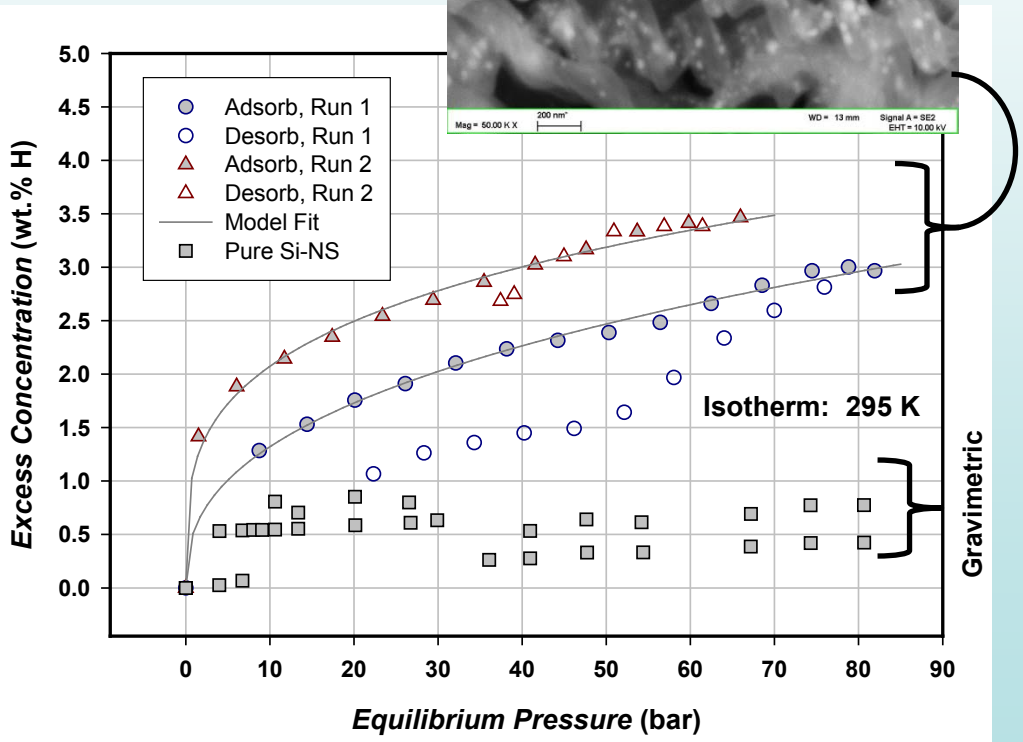
Hydrogen Uptake in Pd-Doped Silica Nanosprings

- Enhanced hydrogen uptake at room temperature is observed in Pd/Si-nanosprings, 3.5 wt.% at 66 bar via volumetric analysis as compared with pure Si-nanosprings (Si-NS)
- This enhanced uptake may be due to chemisorptive absorption via spillover
- Laser-induced thermal desorption mass spectrometry (LTDMS) employed to assess stable binding sites
- Further study and validation is needed

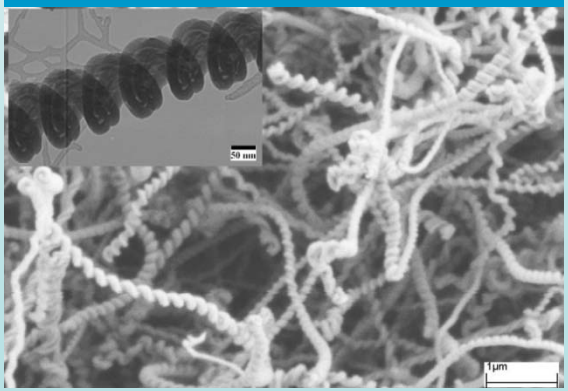
Pd-Doped Silica Nanosprings



Pd Clusters on Si-NS

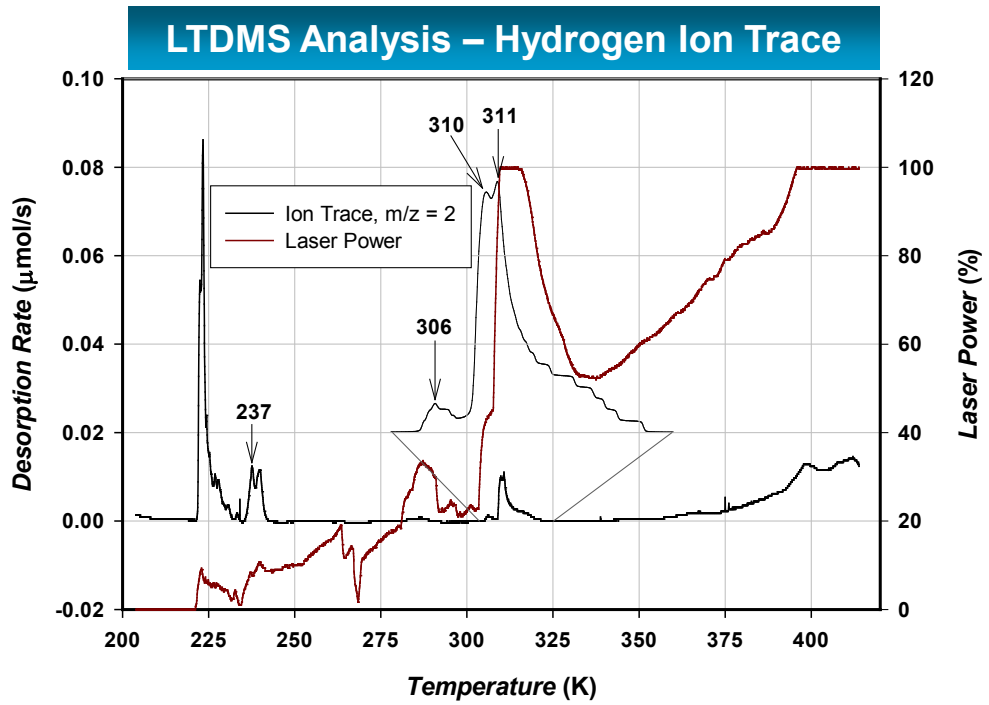


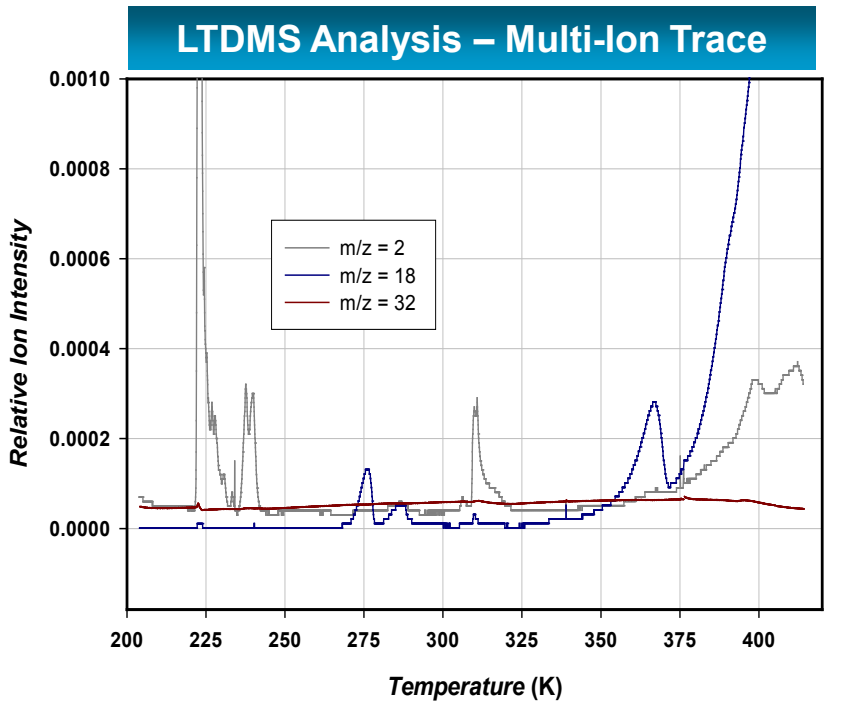
Pure Silica Nanosprings



Accomplishments – External Collaboration

Resolving the Stable Binding Sites in Pd-Doped Silica Nanosprings





- LTDMS analysis reveals multiple, stable binding sites for hydrogen between 306 and 311 K (left plot)
- Relative increase in laser power in the 306-311 K desorption region indicates that desorption of H_2 from Pd/Si-NS is purely endothermic process, and cannot be attributed to an exothermic surface reaction that incidentally forms and liberates molecular hydrogen
- Desorption of water is also evident in multi-ion trace (right plot), but does not occur in 306-311 K region for hydrogen desorption
- Detection of high energy binding sites suggests chemisorptive uptake via hydrogen spillover

Future Work (FY10)

National Testing Laboratory for Solid-State Hydrogen Storage Technologies

Sample Analysis Backlog (Revised 04/09/2010)

Southwest Research Institute

Completed
Underway

nr = not received
na = not applicable
LTDMS = Laser Thermal Desorption Mass Spectrometry

Sample No.	Organization / Collaborator	Sample Type	Analysis	Date Received	Scheduled Start Date	Estimated Completion Date	Priority	Comments
1	Mich. Tech.	Carbon/Piezo Charge	Vol. sorption isotherms, 77 K, Kinetics	8/4/2009	8/6/2009	10/22/2009	High	DOE Directive
2	WSU/GoNano Tech.	Pd-Doped Silica Nanosprings	LTDMS / Volumetric, 295 K	9/17/2009	12/3/2009	1/15/2010	Med	Independent Collaboration
3	Duke	Carbon	Volumetric, 77 K	3/25/2010	4/5/2010	4/23/2010	High	DOE Directive
4	NREL	Carbon	Volumetric, 77 K	4/5/2010	4/26/2010	4/30/2010	High	DOE Directive
5	WSU/GoNano Tech.	TiO2-Doped Silica Nanosprings	LTDMS / Grav. / Vol., 295 K	9/17/2009	2/15/2010	5/7/2010	Med	Independent Collaboration

Summary

- No experimentally meaningful differences were observed by SwRI in hydrogen uptake between carbon samples in which excess charge was induced by embedding piezoelectric elements and the uncharged state (materials provided by Michigan Tech. Univ.).
- In partnership with the EU's NESSHY program, Round-Robin Testing of a $NaAlH_4$ ($CeCl_3$ catalyzed) sample among seven participating laboratories showed significant scatter in the combined results, thus motivating the need for further improvements in standard practices employed by different laboratories.
- Under SwRI's internal research activities, $AuAl_2$- and AuLi intercalated IRMOF-16 were successfully synthesized in an effort to overcome the duffusion-limited kinetics associated with spillover effects, and to explore alternative nano-scale catalysts. $AuAl_2$-IRMOF-16 demonstrated hydrogen uptake at room temperature (1.1 wt.% at 80 bar), achieving steady-state conditions within 15 min. This uptake occurred with only 0.133 wt.% of intercalated catalyst.
- Pd-doped silica nanosprings exhibit promising hydrogen storage properties, achieving up to 3.5 wt.% at 66 bar at room temperature. LTDMS measurements confirmed the occurrence of multiple, stable binding sites. However, further study and validation is needed due to the analytical challenges associated with the physical form of the materials evaluated thus far.