Standardized Testing Program for Solid-State Hydrogen Storage Technologies

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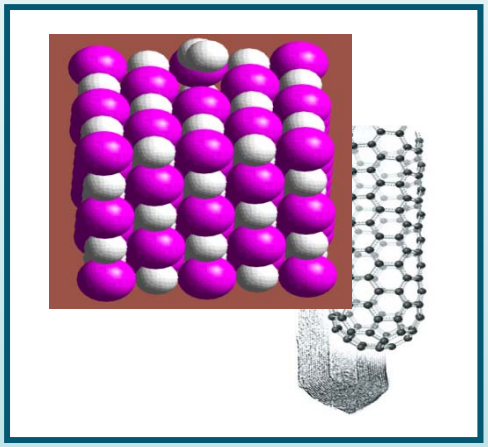


DOE Annual Merit Review, Washington DC
May 18-22, 2009

This presentation does not contain any proprietary or confidential information

Project STP_45_Miller

Overview

DOE Hydrogen Program

Timeline

Phase I

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

Phase II

- Program Start: October 2006
- Program End: September 2011
- 50% 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 FY08: $375k
- Funding Received in FY09: $0

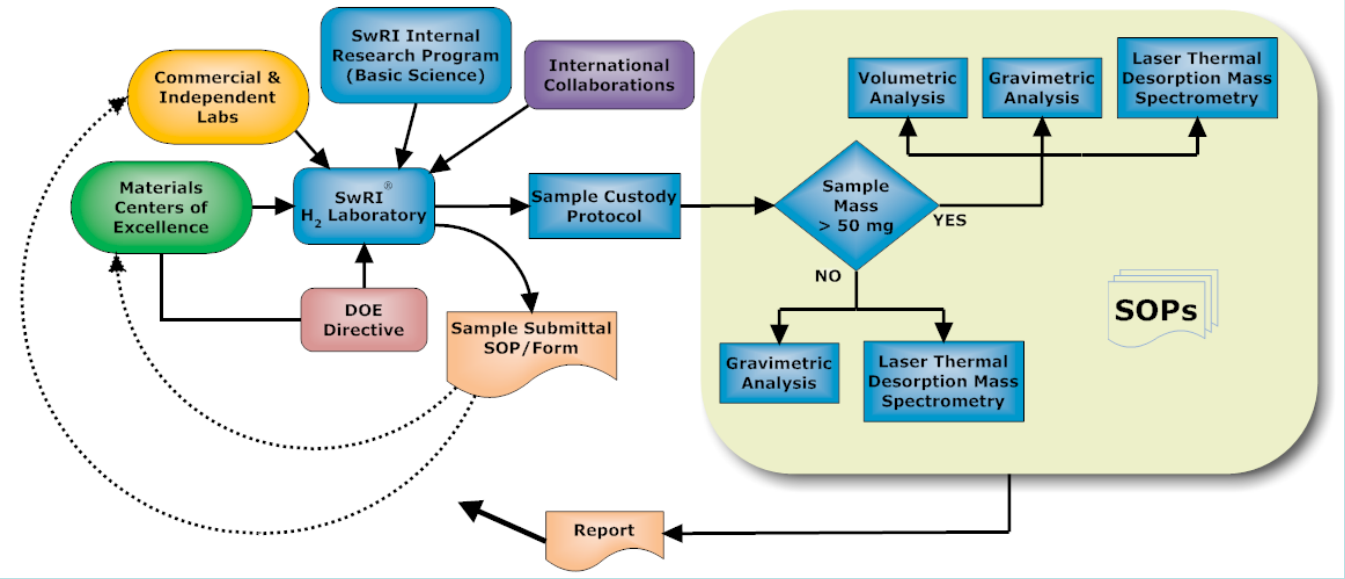
Partners / Collaborations

- Ovonic Hydrogen Systems (Full-scale storage systems)
- INER (Taiwan)
- NESSHY (EC-JRC)
- U. Michigan
- U. Texas at San Antonio
- Washington State University

Objectives - Relevance

Overall

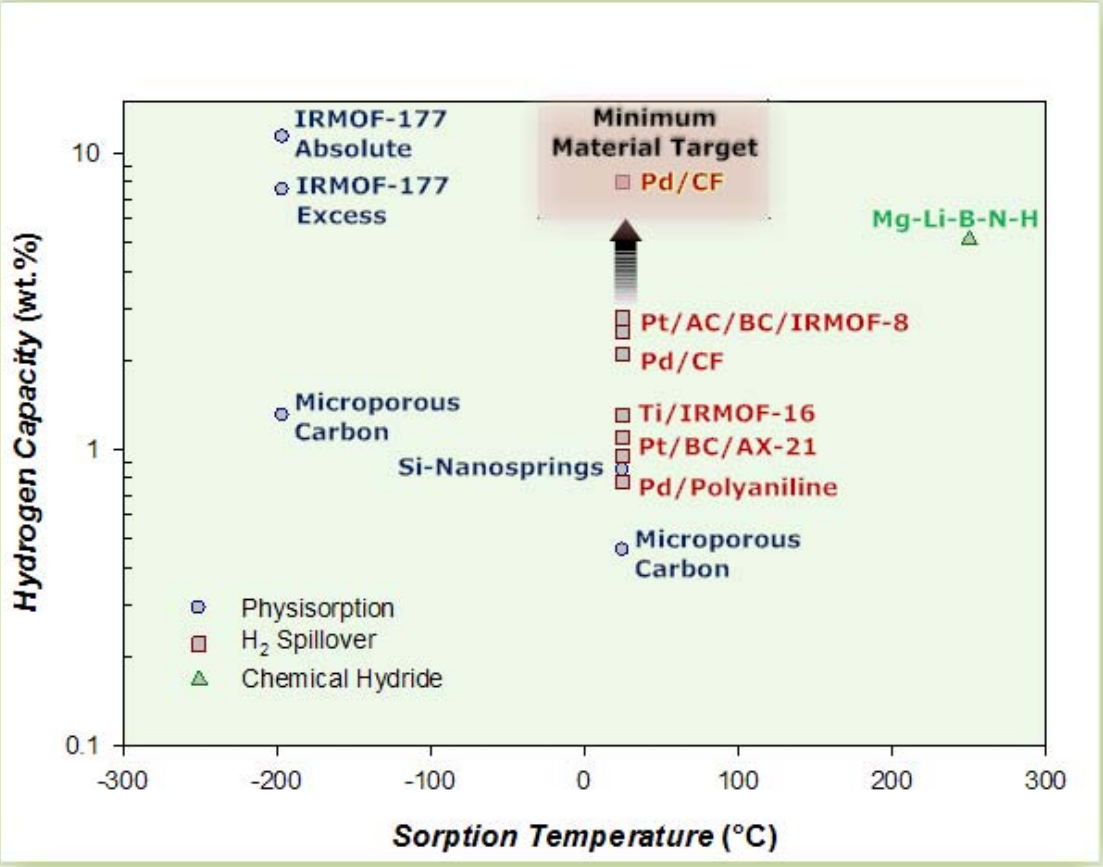
- Support DOE's Hydrogen Storage Program by operating an independent national-level laboratory aimed at assessing and validating the performance of novel and emerging solid-state hydrogen storage materials and full-scale systems
- Conduct measurements using established protocols to derive performance 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

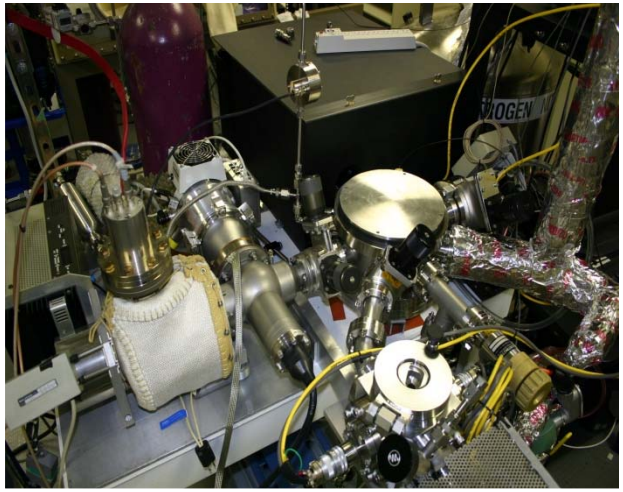
- Evaluate and validate the sorption capacity and kinetics of Mg-Li-B-N-H storage materials
- Evaluate the sorption capacity of Pd-doped polyaniline storage materials
- Further assess hydrogen spillover phenomena in metal-doped carbon foam (CF) storage materials
- Assess hydrogen spillover in metal-intercalated MOF (IRMOF-16) storage materials
- Continue Round-Robin testing in collaboration with the EU's hydrogen storage program (NESSHY)



Milestones

DOE Directives

- Evaluated the Sorption Properties of Pd/Polyaniline — 02/13/2009
- Evaluated the Sorption Capacity, Kinetics, and Stability of Mg-Li-B-N-H — 03/18/2009



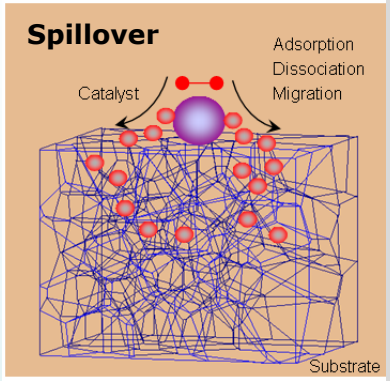
EU (NESSHY) Collaboration

- Participated in Assessing Hydrogen Spillover in New Batch of Metal-Doped Carbon Foam (CF-3) via Inelastic Neutron Scattering Measurements — 07/14/2008
- Evaluated the Sorption Capacity of Metal-Doped Carbon Foam (CF-3) via High-Pressure Volumetric Analysis — 10/20/2008
- Conducted Round-Robin Testing on Alanate Sample in Collaboration with the EU's NESSHY Program — 12/12/2008
- Evaluated Hydrogen and Deuterium Spillover in PdHg-Doped Carbon Foam (CF-1) via Laser Thermal Desorption Mass Spectrometry — 03/03/2009

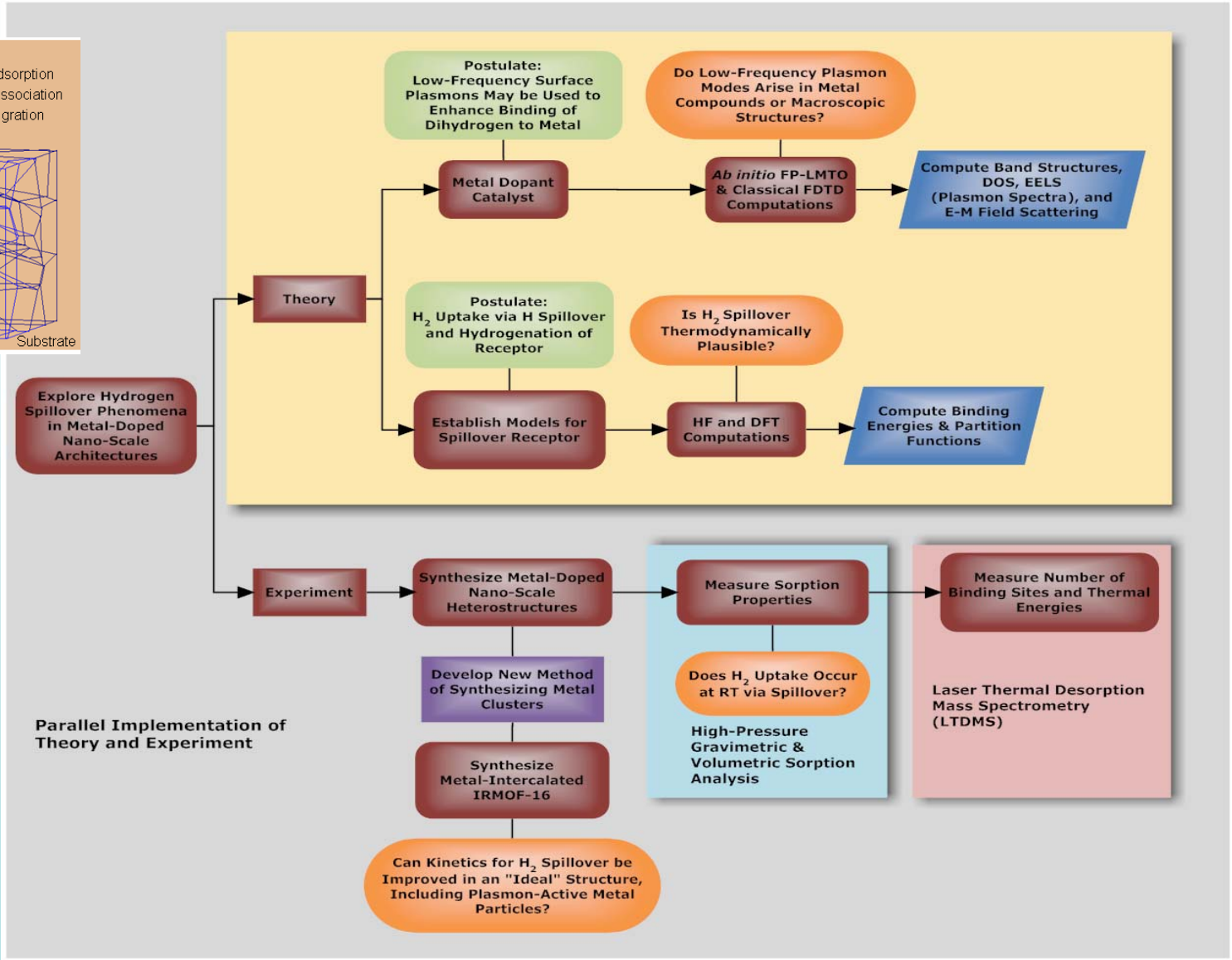
Internal / External Research

- Synthesized Metal-Intercalated IRMOF-16 for H_2 Spillover — 09/16/2008
- Evaluated the Sorption Properties of Si-Nanosprings — 09/18/2008
- Evaluated the Sorption Properties of Ti- and TiB_2 Intercalated IRMOF-16 — 03/04/2009

Approach – Internal/External Research



Proposed Hydrogen Spillover Mechanism: Adsorption of dihydrogen onto catalytic site, followed by dissociation and migration of atomic hydrogen into nanostructured substrate (receptor)



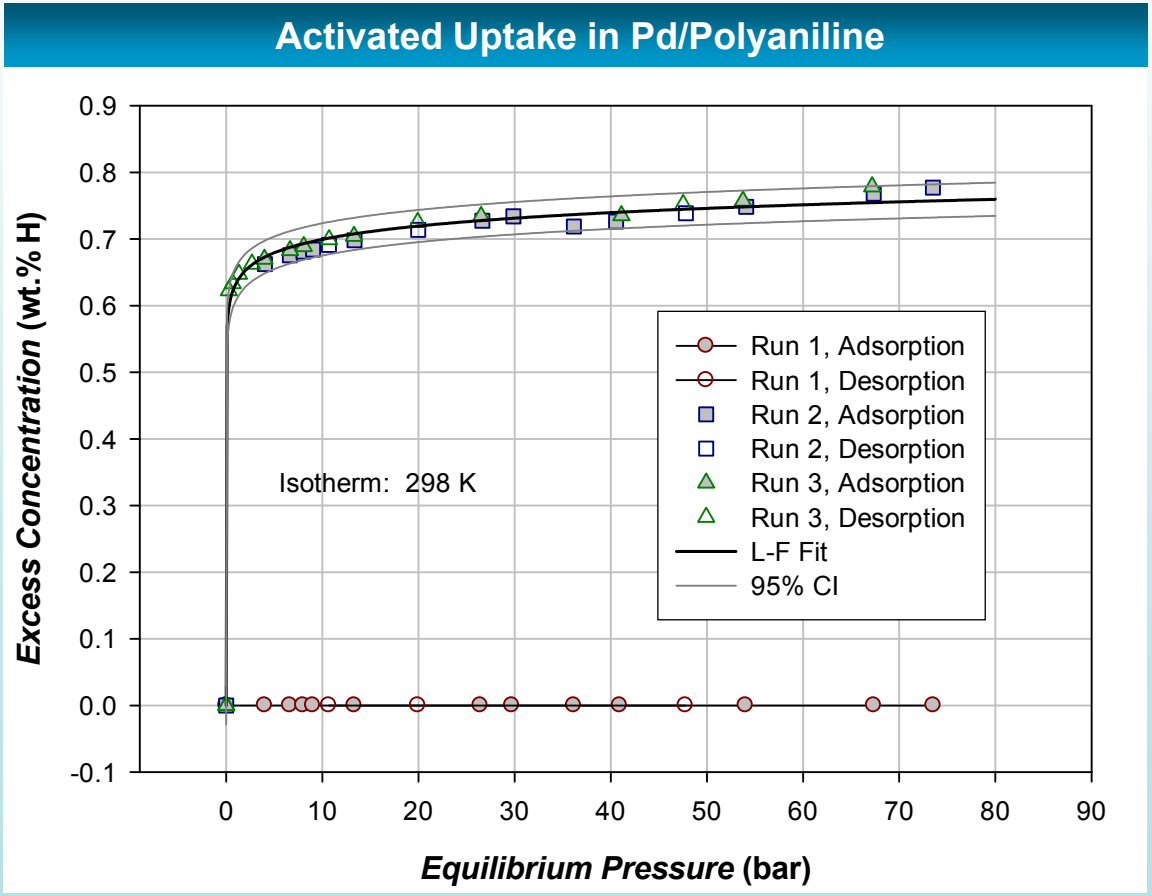
ACCOMPLISHMENTS IN RESPONSE TO DOE PRIORITIES & DIRECTIVES

Accomplishments – DOE Directives

DOE Hydrogen Program

Measurement of H_2 Sorption in Pd-Doped Polyaniline (PANI) Storage Materials (Provided by UNLV)

- Sample preconditioned at 130°C under high vacuum
- No uptake observed during first isotherm at room temperature
- After reconditioning sample at 110°C under high vacuum, second isotherm shows rapid uptake at low pressures (0.6 wt.% at 0.3 bar), reaching maximum uptake at saturation of 0.8 wt.% at 73 bar, which is fully reversible
- Third isotherm yielded same result after reconditioning under similar conditions
- In both cases, weight equilibrium (± 0.01 wt.%) was achieved within 30 min



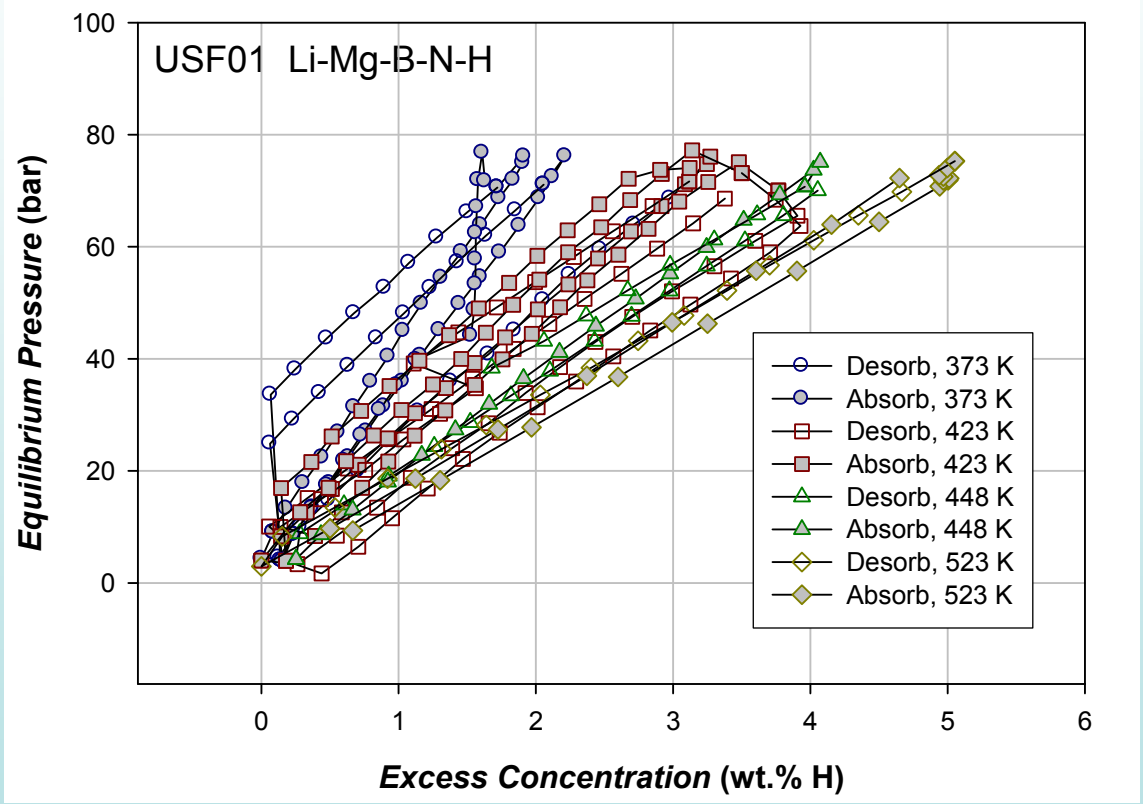
Accomplishments – DOE Directives

DOE Hydrogen Program

Measurement of H_2 Sorption in Mg-Li-B-N-H Storage Materials (Provided by USF)

- Desorption/absorption hysteresis observed at 100°C (373 K), though material becomes fully reversible as temperature is increased
- PCTs do not exhibit a measurable plateau at any temperature
- Maximum reversible uptake occurs at highest temperature, 5.1 wt.% at 75 bar, which is inconsistent with classical metal hydrides
- Results indicate hydride phase formation (transition) in Li-Mg-B-N-H is kinetically limited, giving rise to observed trend

PCT Isotherms for Mg-Li-B-N-H



Note: A large change in heat capacity is suspected for this complex hydride, which would have an influence on the accuracy of results. Calorimetric measurements are needed to quantify this material's isobaric heat capacity through its phase transition(s).

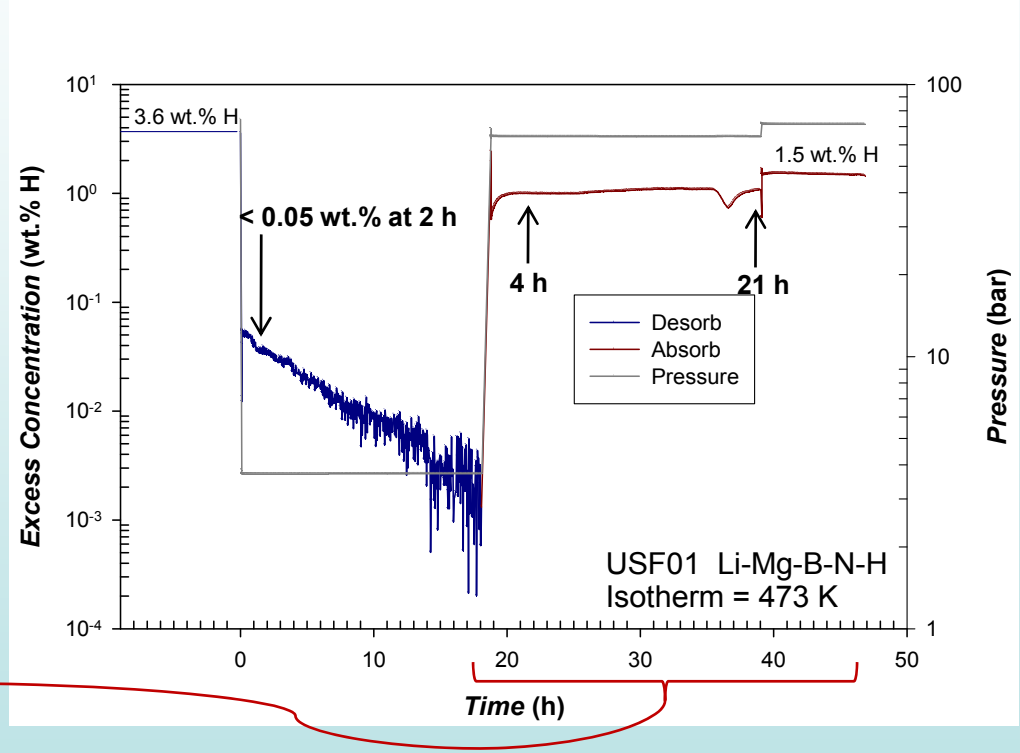
Accomplishments – DOE Directives

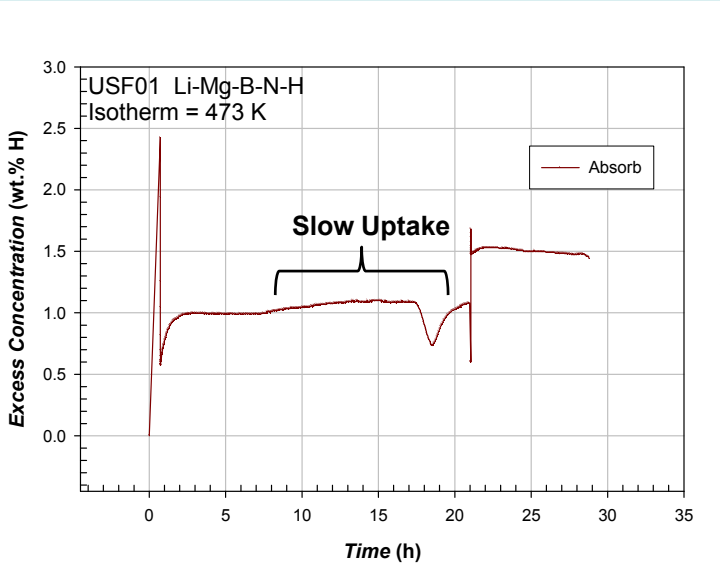
DOE Hydrogen Program

Measurement of H_2 Sorption Kinetics in Mg-Li-B-N-H Storage Materials (Provided by USF)

- Desorption kinetics are faster than absorption, < 0.05 wt.% at 2 hours
- Absorption kinetics exhibit an initial steady-state condition within 4 hours, followed by slow uptake out to 21 hours

Isothermal Kinetics for Mg-Li-B-N-H at 473 K





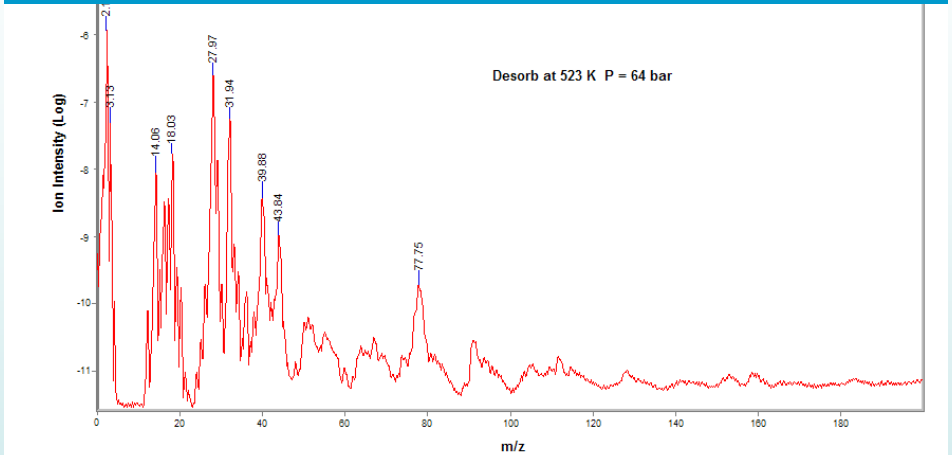
Accomplishments – DOE Directives

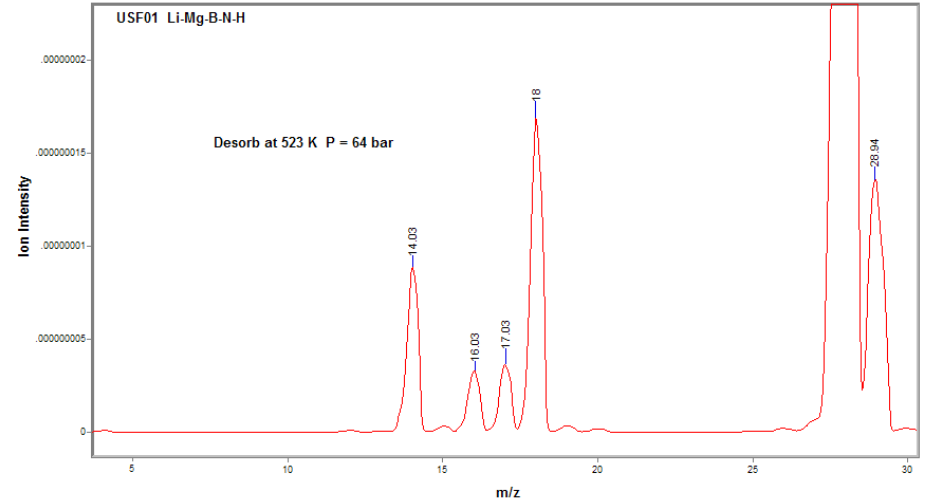
Cycle-Life Chemical Stability of Mg-Li-B-N-H Storage Materials (Provided by USF)

Target Volatile Species	Parent Ion Mass (m/z)	Principal Frag. Ion (Mass)	Occurrence
BH_3^+	13.83	BH_2^+ (13)	X
$B_2H_6^+$	27.67	$B_2H_2^+$ (24) + BH_3^+	X
$B_5H_9^+$	63.13	$B_5H_4^+$ (59)	X
NH_3^+	17.03	100% (17):80% (16): 8% (15): 2% (14): 0.4% (18)	Not in Correct Ratio
$B_3N_3H_6^+$	80.50	$^{11}B_2H_6^+$ (28)	Not Correct Fragment Ions
$C_6H_6^+$	78.11	100% (78):19% (52):19% (51):16% (50):14% (77)	Detected

Volatile species containing boron or nitrogen were not detected during desorption at 523 K, indicating chemical stability in the complex hydride

In Situ Mass Spectrometry During Isothermal Desorption at 523 K



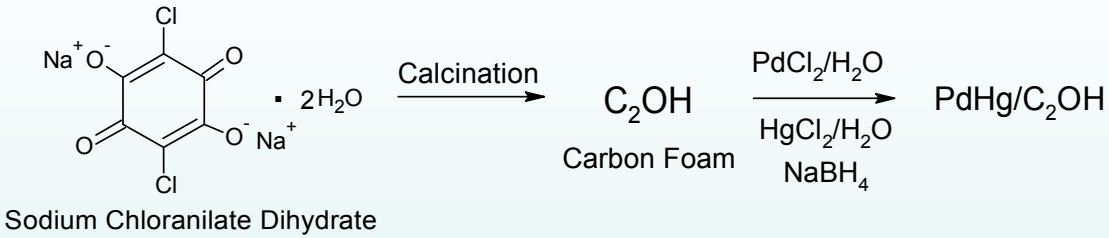


ACCOMPLISHMENTS RELATED TO EU (NESSHY) ACTIVITIES

Accomplishments – EU (NESSHY) Collaboration

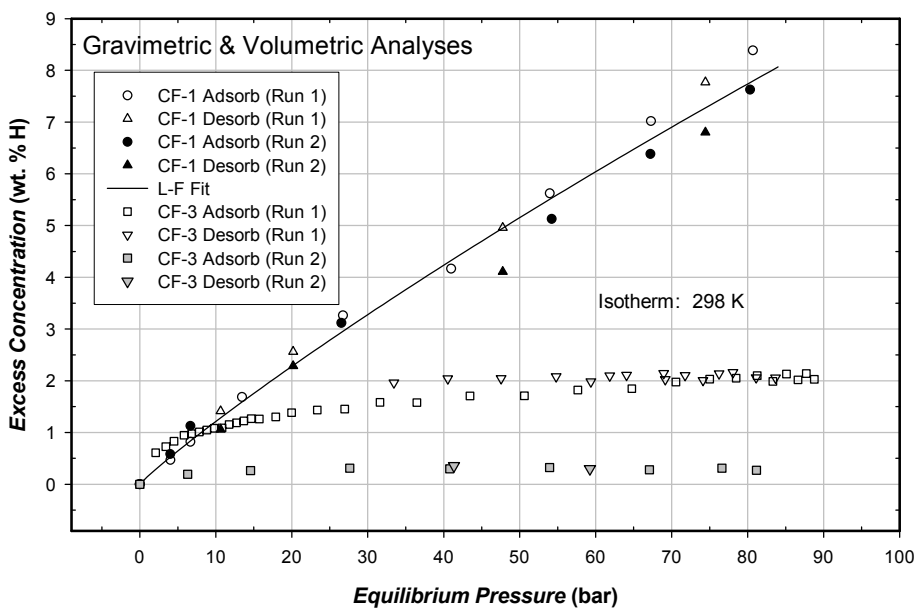
DOE Hydrogen Program

Metal-Doped Carbon Foams for Hydrogen Storage via Spillover



- Second batch of carbon foam (CF-3) provided by Demokritos for parallel studies of H_2 spillover
- Volumetric analyses show lower uptake above 10 bar than previously measured for CF-1, achieving only 2.1 wt.% at 88 bar for CF-3
- However, XRD pattern of CF-3 indicates higher relative intensity of free (unalloyed) Pd than in previous batch (CF-1)
- New batch of PdHg/CF has been synthesized to further study the effects of process variables (additional sorption studies are underway)

Hydrogen Uptake in Two Different CF Samples



Subsequent studies based upon laser induced thermal desorption mass spectrometry (LTDMS) were aimed at examining the catalytic stability of PdHg/CF and resolving stable binding sites

Bourlinos, A. Steriotis, T.; Stubos, T.; Miller, M.A., Zlotea, C., Stubos, A., Steriotis, Th., **2008** (Patent Pending).

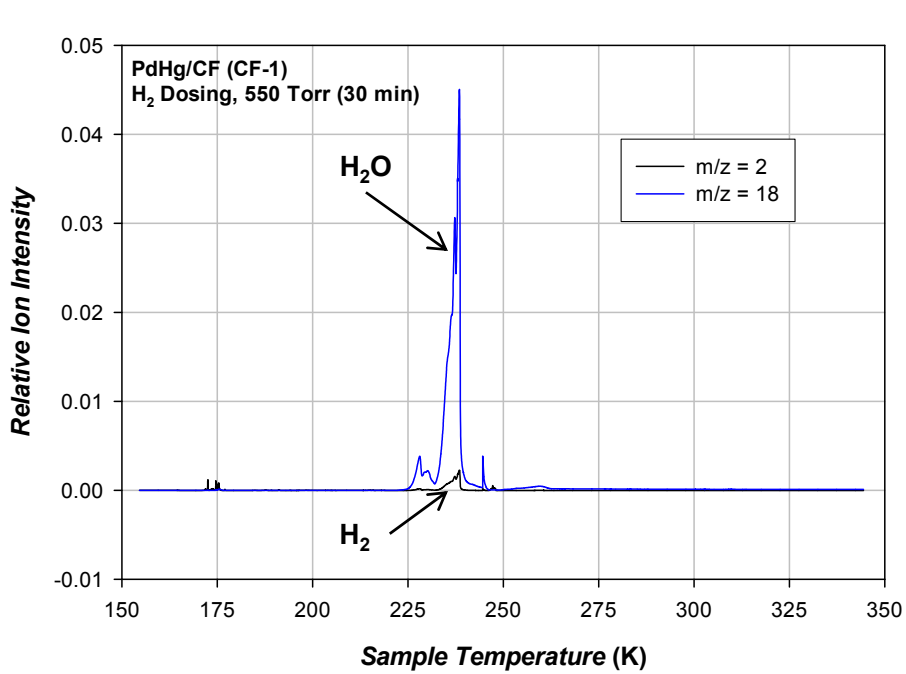
National Center of Scientific Research "Demokritos"

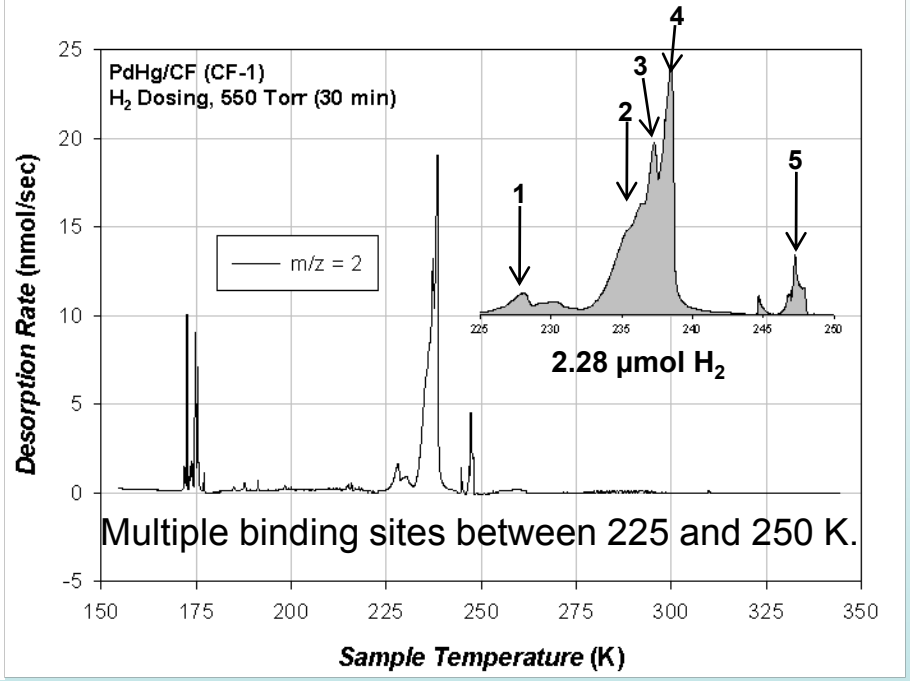
Accomplishments – EU (NESSHY) Collaboration

DOE Hydrogen Program

Resolving Catalytic Stability and Binding Sites in PdHg/CF

LTDMS Desorption Profiles for PdHg/CF (CF-1) Following H_2 Dosing (550 Torr, 30 min)





LTDMS profiles show that a significant quantity of water is desorbed from PdHg/CF compared with hydrogen, likely due to spillover of atomic hydrogen and subsequent binding to oxygen-bearing carbons in CF. Broad range of stable binding sites is also shown.

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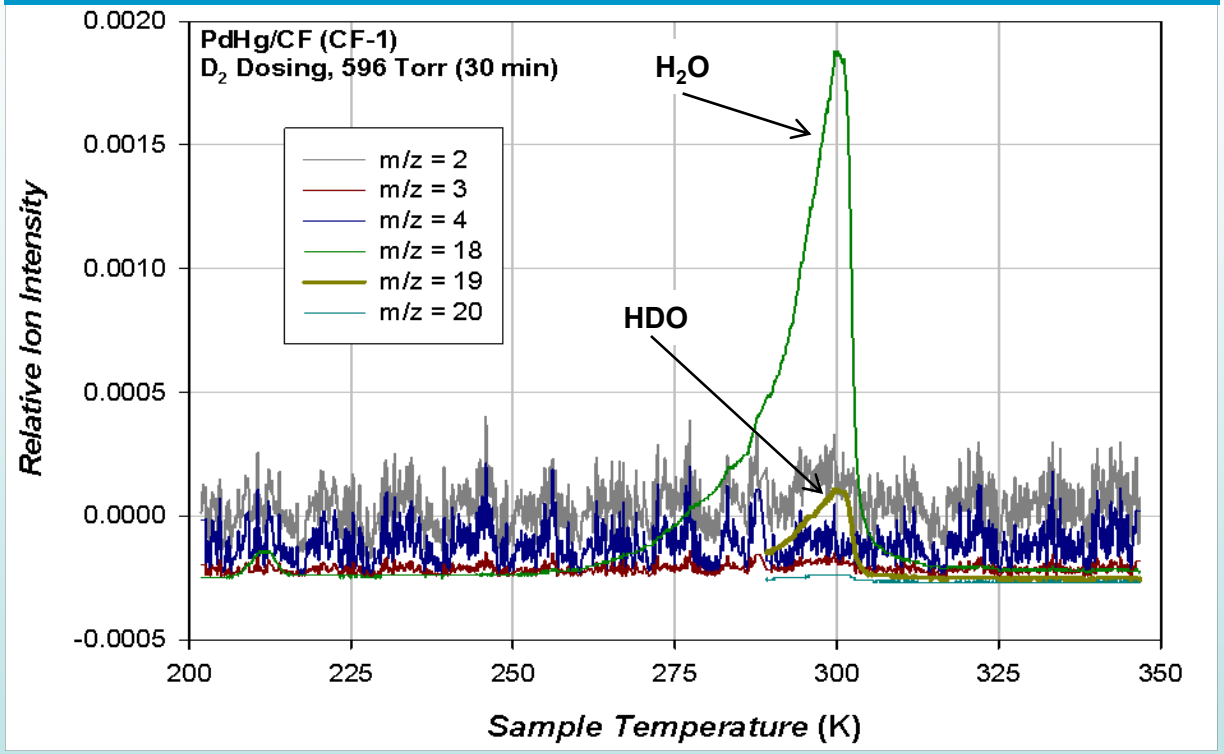
Accomplishments – EU (NESSHY) Collaboration

DOE Hydrogen Program

Resolving Catalytic Stability and Binding Sites in PdHg/CF (Cont.)

LTDMS Desorption Profile Following D_2 Dosing (596 Torr, 30 min)



- Neither D2 nor HD species desorb at detectable levels following deuterium dosing of PdHg/CF
- HDO is desorbed at same temperature as water
- Similar isotopic measurements underway for new batch of PdHg/CF

These results show that D_2 is dissociated by PdHg catalyst and is spilled over onto the CF receptor. Atomic deuterium combines with oxygen-bearing carbons (e.g., -OH), which then desorb as HDO

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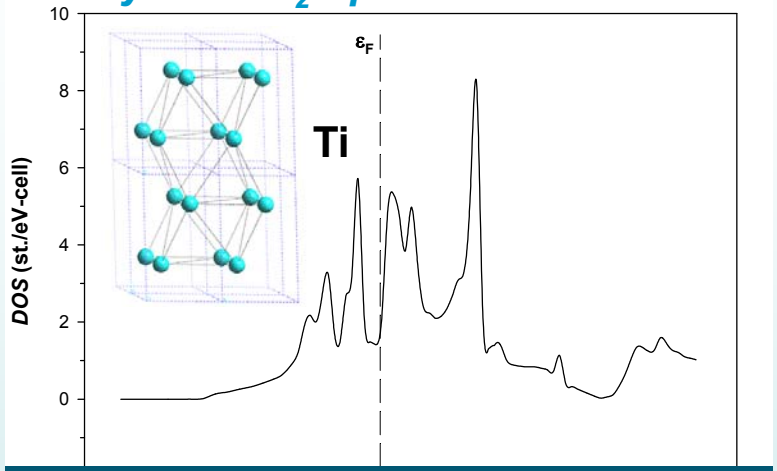
ACCOMPLISHMENTS RELATED TO SWRI®'S INTERNAL & EXTERNAL RESEARCH COLLABORATIONS

Accomplishments – Internal Research

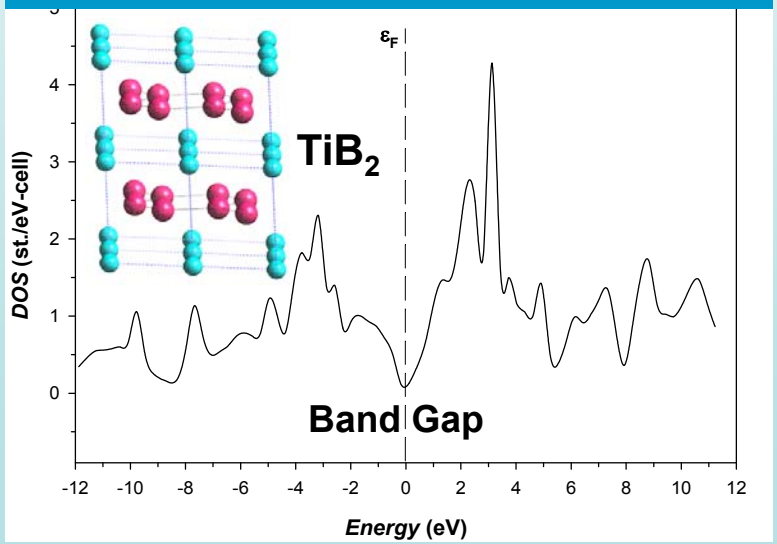
Application of Theory to the Selection of Alternative Catalyst for H_2 Spillover

Goals:

- Select alternative catalysts for intercalating metal organic frameworks (MOFs) and effecting hydrogen uptake via spillover with enhanced kinetics
- Compute density of states using FP-LMTO theory of candidate pure metals and metal compounds
- Choose complementary systems:
  - Pure metal ⇒ conducive to H_2 dissociation
  - Complementary metal compound exhibiting band gap in the density of states (DOS) ⇒ not conducive to H_2 dissociation
- Synthesize metal-intercalated MOFs
- Measure hydrogen uptake in each complement



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

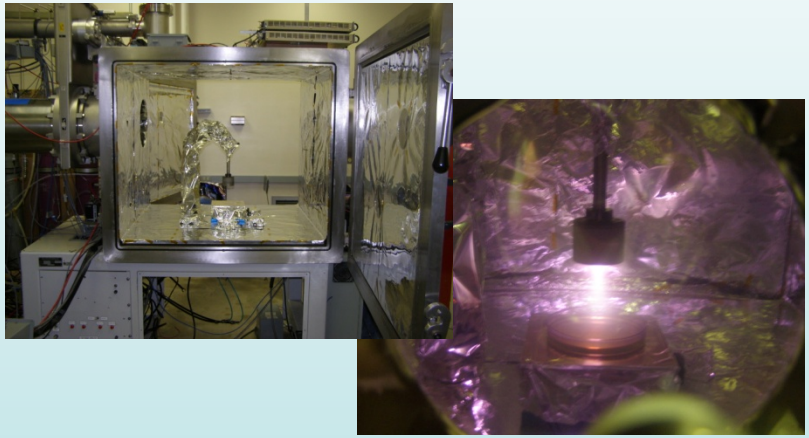


Accomplishments – Internal Research

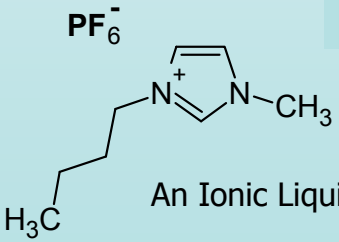
Synthesis of Metal-Intercalated MOFs for Hydrogen Storage via Spillover

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

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



View through viewport of vacuum chamber



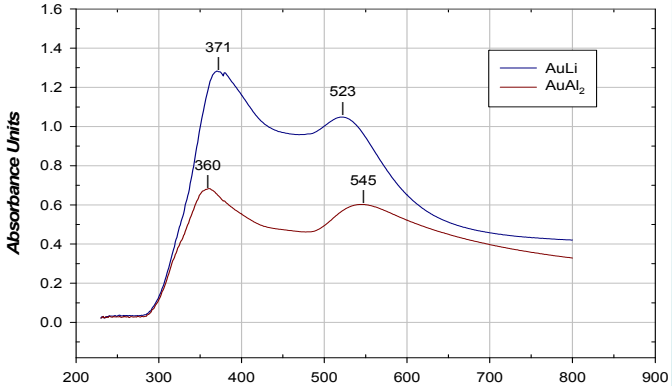
An Ionic Liquid (IL)

Non-Aggregating Metal Clusters in IL Pool

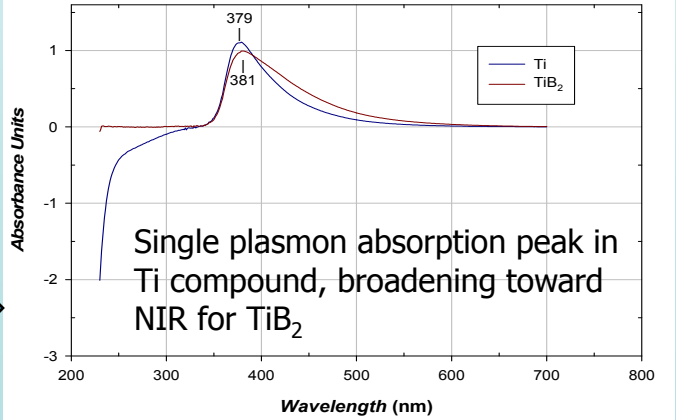
AuLi and $AuAl_2$ Clusters

Metal systems selected for current work: Ti and TiB_2

UV-VIS Absorption Spectra



Gold compounds exhibit two plasmon absorption peaks (probably due to quadrupole resonance), second one extends into the NIR as predicted by theory!



Single plasmon absorption peak in Ti compound, broadening toward NIR for TiB_2

Accomplishments – Internal Research

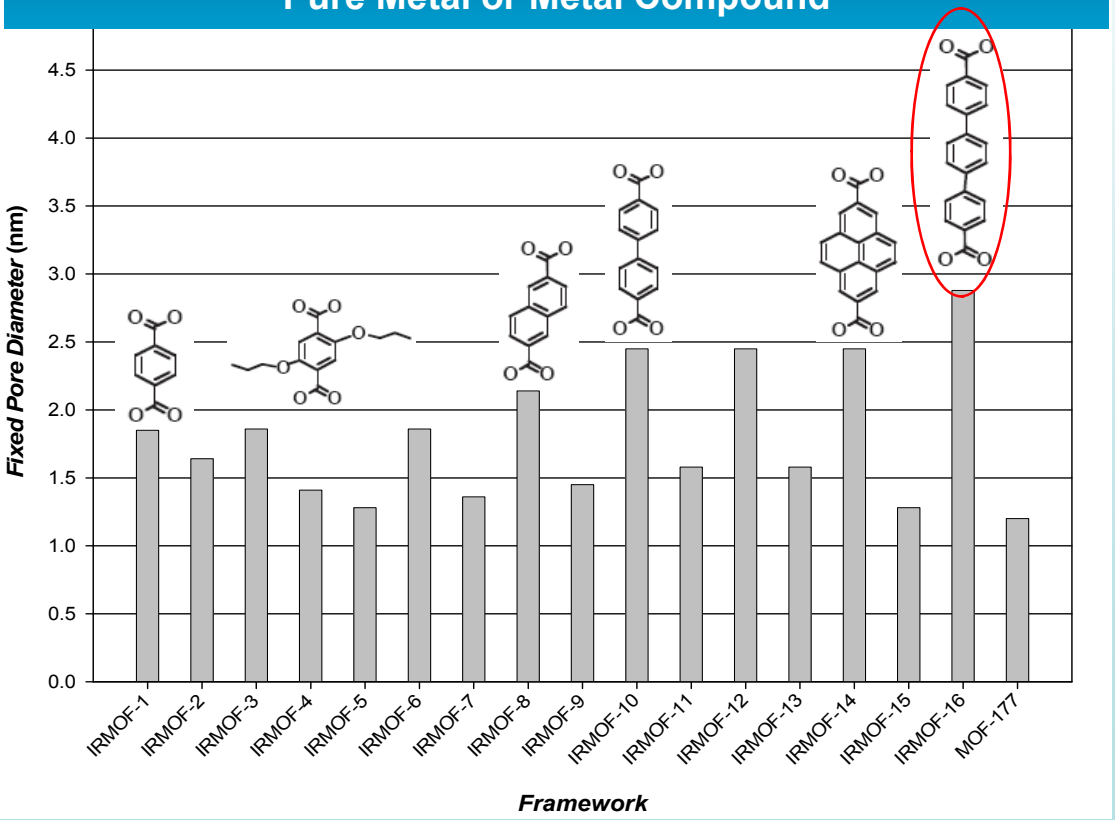
DOE Hydrogen Program

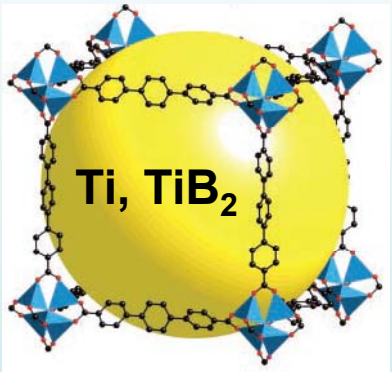
Synthesis of Metal-Intercalated MOFs for Hydrogen Storage via Spillover

Step 2 – In-Situ Intercalation of Metal Particles into Framework

Metal Clusters (~3 nm diam) + MOF Linker + $Zn(NO_3)_2$ $\xrightarrow{IL}$ Metal-Intercalated MOF

Selecting an Appropriate MOF to Accommodate Clusters of Pure Metal or Metal Compound



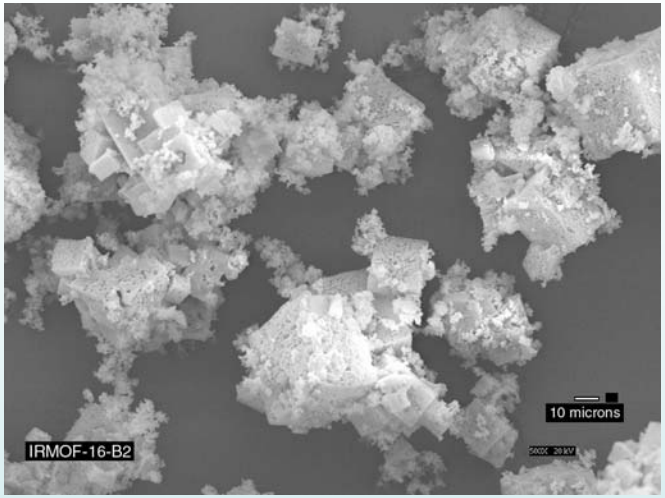


Average cluster diameter practically synthesized: ~3 nm

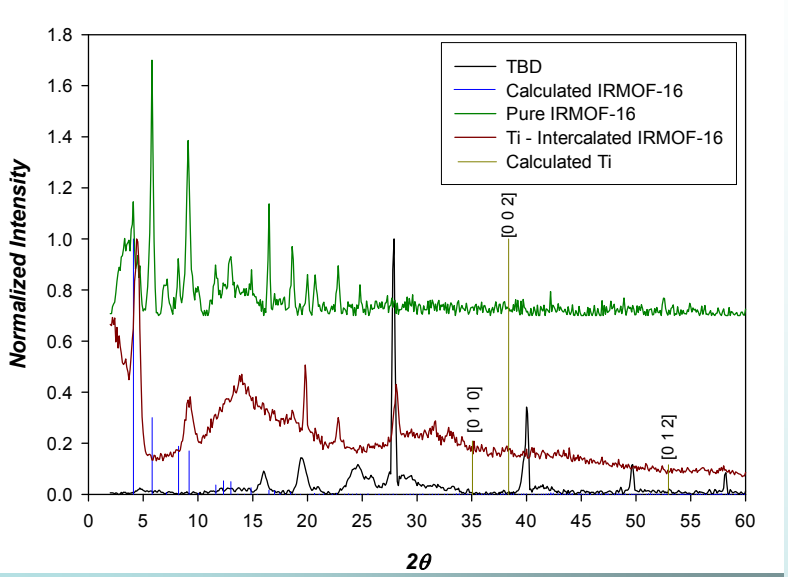
MOFs exhibiting large pore diameters: IRMOF-16 (TPDC linker), 2.9 nm vs. 1.2 nm for MOF-177

Accomplishments – Internal Research

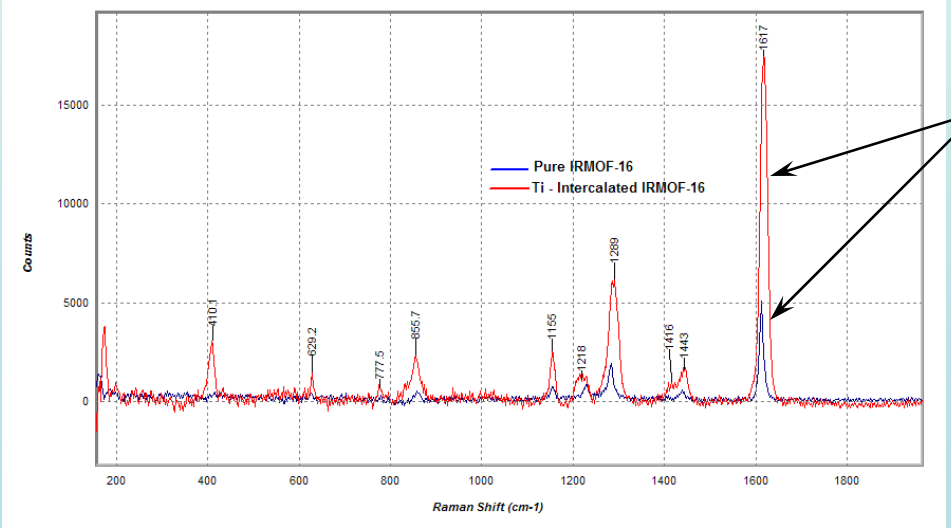
Characterization of Ti-Intercalated IRMOF-16



SEM Image of Ti-Intercalated IRMOF-16



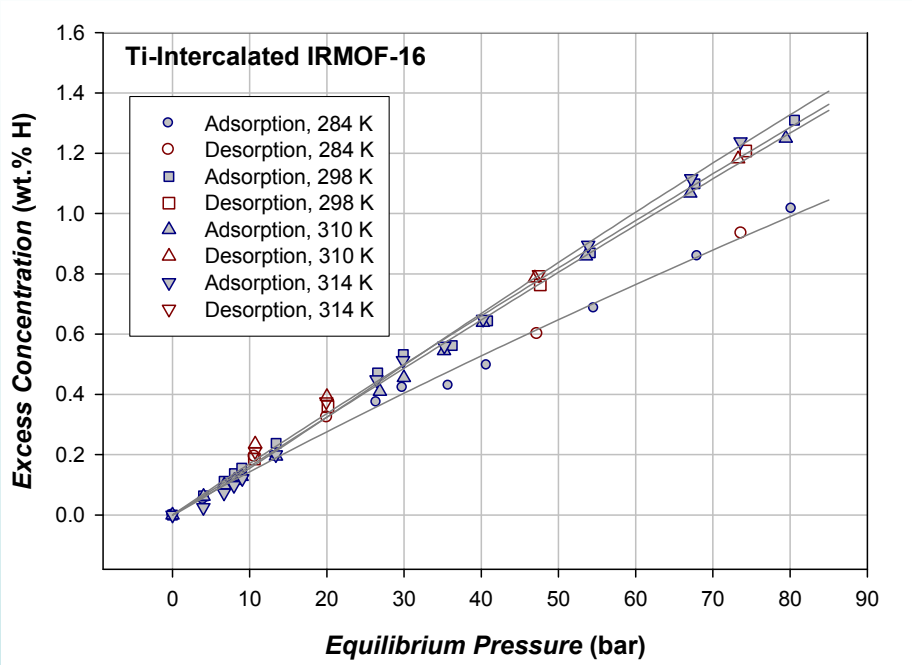
Measured and Calculated PXRD Patterns

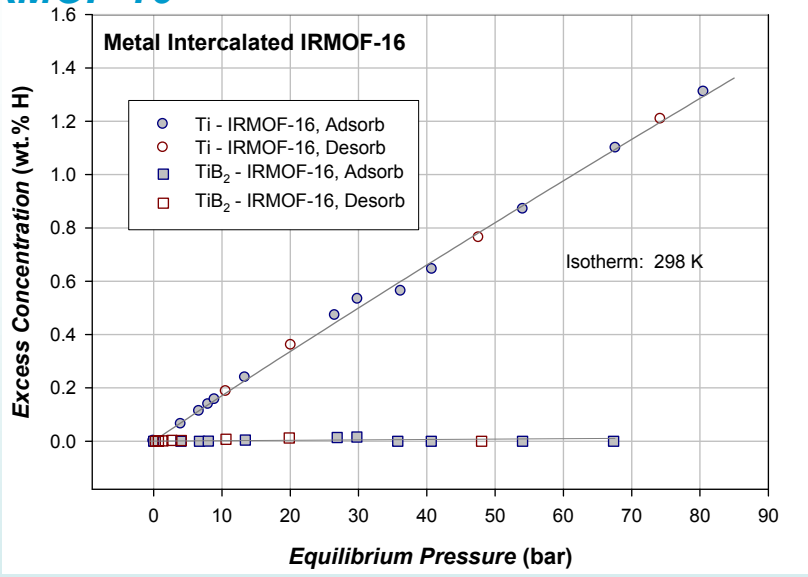


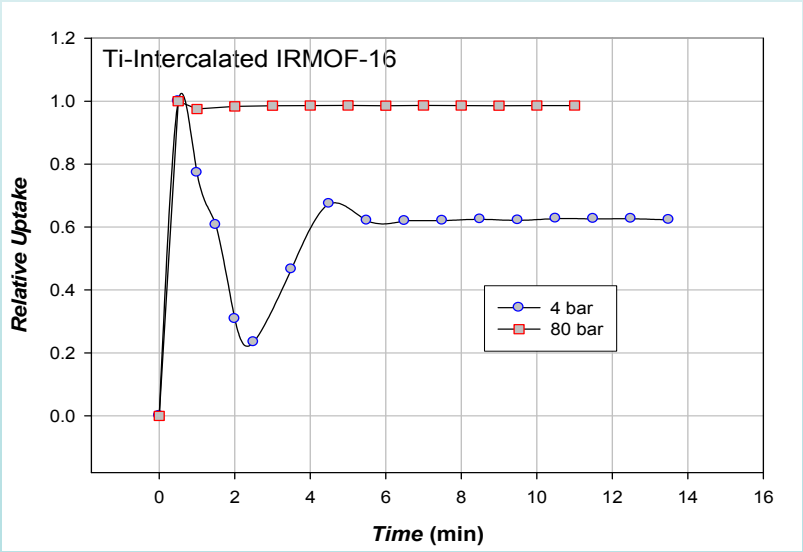
Raman spectrum reveals interesting spectral enhancement effects. Not expected for Ti since plasmon frequency is much higher than NIR laser frequency. Such effects are postulated to be related to cooperative multipole coupling of surface plasmons of Ti particles in the three-dimensional periodic void-structure of the framework

Accomplishments – Internal Research

Hydrogen Uptake in Ti- and TiB_2 Intercalated IRMOF-16







- Enhanced hydrogen uptake at room temperature via spillover is observed without precious-metal catalyst (Ti-IRMOF-16), 1.3 wt.% at 80 bar
- No measurable uptake observed for TiB_2-IRMOF-16 due to band-gap in DOS
- Fast spillover kinetics compared with other materials studied (~ 14 min vs. 600 min for Pt/AC/BC/IRMOF-8)

Future Work (FY08)

DOE Hydrogen Program

National Testing Laboratory for Solid-State Hydrogen Storage Technologies

Sample Analysis Backlog (Revised 01/29/2009)

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	SwRI	TiB2-Intercalated IRMOF-16 Spillover	Grav. sorption isotherms, 284, 298, 310, 314 K, kinetics	na	3/2/2009	3/27/2009	Med	Internal Research
2	Demokritos (NESSHY)	PdHg/CF Spillover	Vol. sorption isotherms, kinetics; LTDMS, binding energies	2/2/2009	3/20/2009	4/24/2009	High	Independent collaboration
3	SwRI	AuAl2-Intercalated IRMOF-16 Spillover	Grav. sorption isotherms, 284, 298, 310, 314 K, kinetics	na	3/31/2009	4/10/2009	Med	Internal Research
4	WSU/GoNano Tech.	Si-Nanosprings	Grav. sorption isotherms, 200-298 K, kinetics; LTDMS, binding energies	2/26/2008	4/13/2009	4/24/2009	Med	Independent collaboration
5	NESSHY	MgH2 + Transition Element	Vol. sorption isotherms, 553 & 593 K, kinetics, dissociation enthalpy	3/26/2008	4/27/2009	5/22/2009	Med	Round-Robin Testing with EU
6	SwRI	LaNi5 Platelet Technology	Vol. sorption isotherms, 298 - 398 K, kinetics, dissociation enthalpy	na	5/25/2009	6/5/2009	Med	Internal Research
7	SwRI	CNT Platelet Technology	Grav. sorption isotherm, 298 K, LTDMS	na	4/27/2009	5/8/2009	Med	Internal Research

Summary

DOE Hydrogen Program

- Pd-doped polyaniline (PANI) provided by UNLV exhibited reversible hydrogen uptake of 0.8 wt.% at 73 bar at room temperature with fast kinetics.
- Mg-Li-B-N-H complex hydride provided by USF was shown to exhibit reversible uptake at temperatures above 150°C with uptake being proportional to temperature. A maximum uptake of 5.1 wt.% was observed at 250°C and 75 bar without evidence of any chemical instability. Hydride phase formation in Li-Mg-B-N-H is thought to be kinetically limited.
- In collaboration with Demokritos (NESSHY), resumed efforts to further explore hydrogen spillover in PdHg-doped carbon foams and discern process variables in the synthesis of these materials. A second batch of material exhibited lower uptake above 10 bar than previously measured (2.1 vs. 8.0 wt.% at 80 bar), which may be attributed to higher segregation of PdHg catalyst as compared with first batch. Isotopic LTDMS measurements, however, also indicate that spilt over hydrogen binds to oxygen-bearing carbons in CF to evolve water upon desorption. Future experiments are aimed at further assessing this mechanism.
- Under SwRI®'s internal research activities, Ti- and TiB_2 intercalated IRMOF-16 were successfully synthesized in an effort to overcome the diffusion-limited kinetics associated with spillover effects, and to explore alternative nano-scale catalysts. Ti-IRMOF-16 demonstrated hydrogen uptake at room temperature (1.8 wt.% at 80 bar), achieving steady-state conditions within 14 min.