

IV.E.7 Standardized Testing Program for Solid-State Hydrogen Storage Technologies

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Objectives

Overall

- Support DOE's Hydrogen Storage Program by operating an independent, national-level reference 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.

Current

- Provide an in-depth assessment and validation of hydrogen spillover in Pt/AC/BC/IRMOF-8 and Pt/AX-21 compounds.

- Assess hydrogen adsorption and spillover phenomena in catalytically-doped carbon foam.
- Evaluate the thermodynamic plausibility of hydrogen spillover in catalytically-doped metal organic frameworks (MOFs).
- Continue round-robin testing in collaboration with the European Union's (EU's) Novel Efficient Solid Storage of Hydrogen (NESSHY) program.

Technical Barriers

The technical barriers associated with the operational objectives of the laboratory are:

- Standardization of methods suitable to a wide variety of compositions of matter.
- Development and implementation of "Gold Standard" measurement techniques.

Moreover, this project addresses the following technical barriers from Section 3.3.4.2 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Verification of material performance:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Verification of system performance:

- (K) System Life-Cycle Assessment
- (Q) Reproducibility of Performance
- (F) Codes and Standards

Technical Targets

This project addresses the fundamental need for establishing a national-level laboratory whose core mission is to study and independently verify the intrinsic sorption characteristics of novel and emerging materials for hydrogen storage, including such activities as they pertain to their use in full-scale storage systems. As a fully qualified laboratory under the purview of the DOE, the laboratory plays a central role in down-selecting materials and systems that emerge from the Centers of Excellence and outside entities by:

- Providing in-depth analysis and understanding of hydrogen physisorption and chemisorption mechanistic behavior.

- Determining and validating material and system storage capacities.
- Determining material and system kinetics (charging/discharging rates), thermodynamics, and cycle-life durability.
- Contributing to the testing requirements for codes and standards of full-scale systems.
- Providing listing and labeling services for full-scale systems such as fire safety performance.

Accomplishments

- Evaluated hydrogen spillover effects in Pt/AX-21 and verified 1.1 wt% hydrogen uptake at 298 K and 75 bar.
- By leveraging SwRI's parallel research activities, the thermodynamic plausibility of hydrogen spillover in catalytically-doped IRMOF-8 was investigated by employing experimental methods based on laser-induced thermal desorption mass spectrometry (LTDMS) and theoretical computations at the level of Hartree-Fock (HF) and density functional theory (DFT).
- Developed theoretical foundation for the role of low-frequency surface plasmons in the binding interactions of dihydrogen on clusters of gold and titanium compounds, leading to rational designs for new storage materials with high room-temperature uptake via spillover.
- In collaboration with the National Center of Scientific Research “Demokritos” in Greece (NESSHY), a new structural motif based on carbon foam and PdHg catalyst was developed which yielded high reversible hydrogen uptake (8 wt% at 80 bar) at room temperature via what is believed to be a spillover mechanism.
- Completed round-robin testing on ultra-microporous carbon in collaboration with the EU's NESSHY program.



Introduction

The principal obstacle to the implementation of a safe, low-pressure hydrogen fueling system for fuel cell powered vehicles remains storage under conditions of near-ambient temperature and moderate pressure. While many approaches to this problem have to date focused on materials for physisorption of dihydrogen, wherein useful uptake is realized only at low temperatures (e.g., 77 K), recent experiments have suggested the possibility of chemisorptive strategies based on hydrogen spillover. Of particular note has been the work of Yang and coworkers [1,2], where their approach has made use of spillover of hydrogen

chemisorbed on catalytic metal surfaces onto amorphous and crystalline substrates. Other researchers, including our laboratory, have focused their efforts on elucidating the spillover mechanism in heterostructures of this kind [3]. Though still elusive, the mechanism seems to entail: (1) adsorption of dihydrogen on the surface of the metal catalyst; (2) dissociation of dihydrogen and chemisorption of atomic hydrogen on the surface; (3) spillover of atomic hydrogen onto the substrate; and finally (4) chemisorptive binding of atomic hydrogen with specific sites on the substrate.

In order to assess critically the viability of hydrogen-storage materials predicated upon spillover, a better understanding of the underlying mechanism is required. This can be only accomplished by establishing the origins of kinetic and thermodynamic effects associated with these types of materials. To achieve these objectives, our laboratory has directed its focus on evaluating materials that have been engineered to exhibit spillover effects, and conducting critical experiments combined with *ab initio* computations toward gaining an understanding of the mechanisms involved. Meanwhile, new structural motifs based on alloy catalysts and low-cost, highly-active carbon substrates have been explored – both theoretically and through experimental validation – culminating in materials with high hydrogen uptake at room temperature via spillover effects.

Approach

Validating the sorption behavior of storage materials and uncovering the mechanisms involved are approached through close collaboration with researchers among the Materials Centers of Excellence (CoE) (e.g., the Physisorption CoE), the international community, and SwRI's Internal Research & Development Program (IR&D) (Figure 1). The laboratory employs a “best practices” approach based on standard operating procedures documented analytical methods to critically evaluate novel storage materials of potential impact to the sought-after storage goals. By leveraging SwRI's IR&D program, fundamental aspects of materials research are addressed where critical knowledge or physical matter is presently lacking. This element of the program provides a venue for the discovery of new materials and the elucidation of unknown mechanisms.

Results

We report the experimental verification of hydrogen chemisorption via spillover on a Pt-catalyzed microporous carbon, AX-21 (Pt/AX-21), and further investigate theoretically this effect in Pt-catalyzed, carbon-bridged IRMOF-8 (Pt/AC/BC/IRMOF-8). Experimental results confirm a spillover mechanism leading to 1.1 wt% uptake at 74 bar for the Pt/AX-21 compound (Figure 2) and 2.5 wt% uptake at 75 bar for

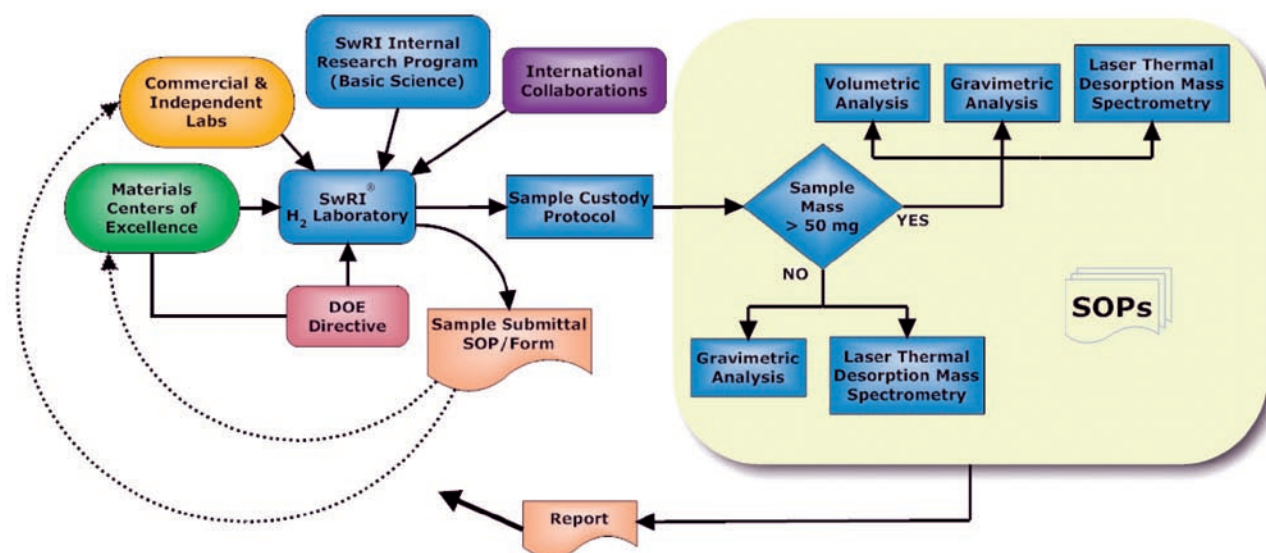


FIGURE 1. Overall Scheme of Laboratory Interactions, Technical Role, and Reporting Process

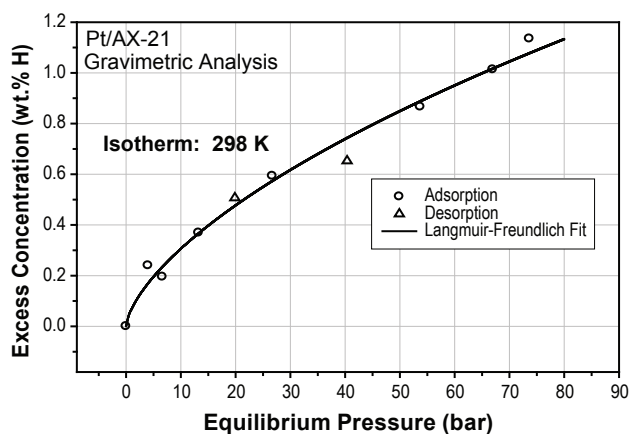


FIGURE 2. High-Pressure Gravimetric Sorption Isotherm Measured for Pt/AX-21 at Room Temperature

the Pt/AC/BC/IRMOF-8 compound, each measured at 298 K. These results are remarkably similar to those previously published by Yang and coworkers [2], showing a nearly linear uptake without achieving saturation below 100 bar. It is important to note that both laboratories observed exceedingly slow uptake kinetics as witnessed by equilibration times for each pressure point in the isotherm of five hours or more.

LTDMS measurements further revealed multiple binding sites occurring between 263 and 298 K, substantially higher than that for simple physisorbed dihydrogen (165 K) [3]. These binding sites collectively occurred well within the reversible chemisorptive regime at room temperature (5-14 kcal/mol). The LTDMS measurements indicate that, while pure IRMOF structures exhibit only weak physisorption interactions between hydrogen and the framework, at

least four binding sites with much stronger interactions are entailed in Pt/AC/BC/IRMOF-8. It is possible to attribute these interactions to chemisorption of hydrogen following dissociation of dihydrogen at catalytic center and spillover of atomic hydrogen onto the framework.

Ab initio calculations were carried out at the level of HF and DFT to elucidate the thermodynamics for the addition of dihydrogen to the organic linker in IRMOF-8, naphthalene-2,6-dicarboxylate (NDC). The associated enthalpies for the sequential addition of one equivalent of dihydrogen are given in Table 1. The results reveal the two levels of theory to be in qualitative agreement with one another. The DFT calculations predict that the first addition of H₂ to be mildly endothermic, corresponding to the disruption of the quasi-aromatic naphthalene system, across the 1 and 4 positions. The second addition across the 2 and 3 positions is found to be exothermic as there is not aromatic penalty to be paid. The third addition must be made to the benzene moiety, and it is, therefore, predicted to be endothermic. Finally, the fourth and fifth additions are both predicted to be exothermic. Total

TABLE 1. Enthalpies (ΔH) of the Addition of Dihydrogen to the IRMOF-8 Model at 298 K and 1 bar (kcal/mol); Organic Linker: NDC = Naphthalene-2,6-Dicarboxylate.

Level of Theory	NDC						Total
	0a	2a	4a	6a	8a	10a	
HF/6-31G(d)	0.0	-2.5	-22.4	4.7	-23.8	-26.6	-70.6
B3LYP/6-31G(d)//HF/6-31G(d)	0.0	3.3	-19.8	9.7	-18.5	-22.1	-47.4

Bond dissociation energy (BDE) of Dihydrogen:
Experiment = 104.2; HF/6-31G(d) = 76.8; B3LYP/6-31G(d)//HF/6-31G(d) = 104.7 kcal/mol.

enthalpies -47.4 and -70.6 kcal/mol are computed for the addition of five equivalents of molecular hydrogen at the DFT and HF levels of theory, respectively. These values correspond to average enthalpies of addition for one equivalent of molecular hydrogen of -9.5 (DFT) and -14.1 (HF) kcal/mol. Overall, the theoretical results suggest the thermochemical plausibility of the spillover mechanism and offer upper limits for chemisorptive uptake in these materials.

The temperature range over which hydrogen was desorbed in the LTDMS measurements (260 – 294 K) for Pt/AC/BC/ IRMOF-8 was transformed to the thermodynamic total energy of the chemical system by calculating the microcanonical partition functions for the hydrogenated NDC structures, which were determined from the *ab initio* calculations. Assuming that the dynamics of NDC in unit cells entail only vibrational internal degrees of freedom, the results indicate that there is good agreement between the combined experimental (LTDMS) and theoretical (*ab initio* calculations), and independently-measured isosteric enthalpies for similar hydrogen concentrations [4].

In view of the potential benefits of spillover mechanisms for achieving high reversible uptake near room temperature, we were motivated to explore at a fundamental level alloy nanostructures (catalysts) that could facilitate binding and spillover of hydrogen. By leveraging IR&D resources, we established the theoretical foundation for how binding interactions between dihydrogen and alloy nanostructures may be influenced by coupling ground-state vibrations of dihydrogen with low-frequency surface plasmons in clusters of the metal compounds of gold (AuLi, AuNa₂, AuB₂, AuAl₂, AuGa₂, and AuIn₂) and titanium (TiB₂) [5]. To examine the proposed plasmon effects, *ab initio* calculations based on the full-potential linear muffin-tin orbital theory were undertaken and the electron energy loss spectra were systematically surveyed to determine whether plasmon contributions arise at low frequencies in these compounds (Figure 3). The calculations showed that AuLi, AuAl₂, and TiB₂ in particular exhibit plasmon-like modes near the ground-state energy of dihydrogen (0.5 eV) which, according to the present theory, would favorably influence the binding energy of adsorbed dihydrogen on the surface of the catalyst. These modes were experimentally confirmed by measuring Raman surface enhancement effects from clusters of these compounds under near-infrared excitation.

The importance of the catalytic properties of binary compounds and the articulation of the catalyst with the underlying substrate was brought to light through a fortuitous collaboration with the National Center of Scientific Research “Demokritos” in Athens, Greece (under the NESSHY program). In this collaboration, a new composite material (*i.e.*, heterostructure) was developed and the sorption properties were determined

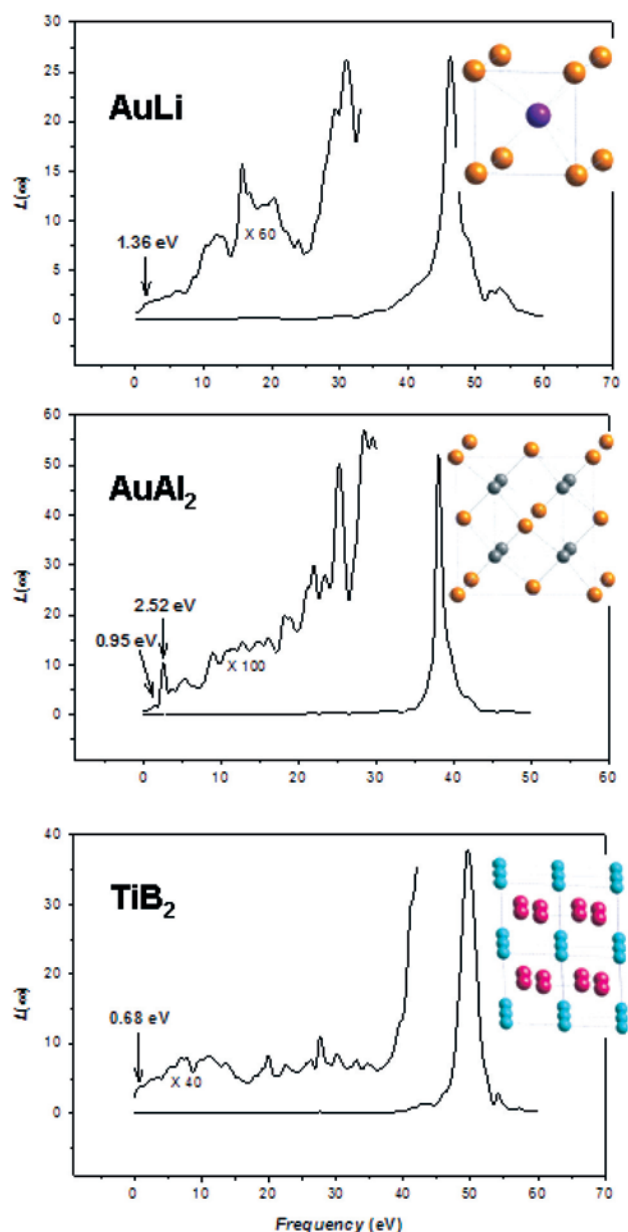


FIGURE 3. Energy-Loss Spectra Theoretically Computed for Gold and Titanium Compounds, Showing Lowest-Frequency Plasmon-Like Modes

gravimetrically. This material comprises a lightweight, low-cost carbogenic foam (CF) with highly active surface-sites (high concentration of radical aggregates), and doped with PdHg (potarite, *P4/mmm*) clusters. While the hydrogen storage capacity of the undoped CF at room temperature was negligible, PdHg/CF revealed a remarkably high sorption capacity of 8 wt% at room temperature and 80 bar, which was observed to be completely reversible (Figure 4). The overall kinetics for adsorption and desorption were, however, exceedingly slow and typically required 5 to 10 hours to reach equilibrium.

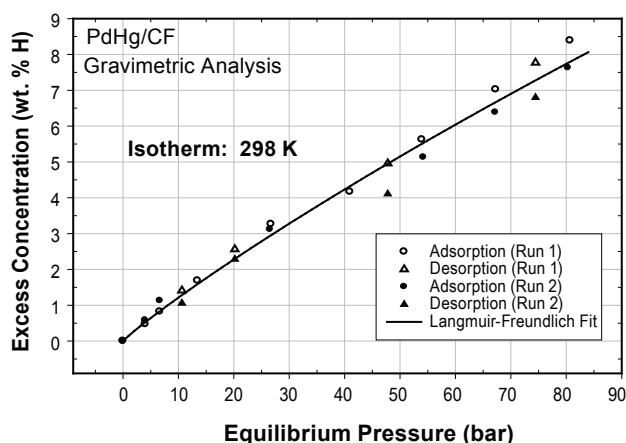


FIGURE 4. High-Pressure Gravimetric Sorption Isotherm Measured for PdHg/CF at Room Temperature

Given the similarities between the nearly linear sorption profiles and slow kinetics observed in PdHg/CF and other heterostructures, such as Pt/AC/BC/IRMOF-8, Pt/AX-21, and Pt/SWNT previously studied in our laboratory, we hypothesize the operative mechanism for hydrogen uptake to be via spillover. Intensive efforts are presently underway to further corroborate the sorption results for PdHg/CF, and to gain a better understanding of the nature of the binding interactions at play.

Conclusions and Future Directions

The potential for chemisorptive strategies via spillover in catalytically-doped nanostructures points to promising opportunities in meeting the DOE on-board storage targets. However, attainment of a broader than present mechanistic understanding of hydrogen spillover in these compounds should be pursued with urgency so that rational designs for new materials with much improved kinetics can be synthesized and evaluated in the near future. Based on the recent results for PdHg/CF, for example, it is evident that much has yet to be learned about what structural motifs are conducive to spillover and why.

Overall, the immediate scientific questions to answer for the collective class of spillover materials under investigation can be summarized concisely: (1) What are the thermodynamic constraints and driving forces for spillover relative to the catalyst and substrate? (2) What is the nature of binding interactions between hydrogen and the substrate after dissociative spillover of dihydrogen from the catalyst? (3) What role does catalyst composition and structure play on surface adsorption, chemisorption, and dissociative spillover of dihydrogen? (4) Are there ideal structural motifs that exhibit high reversible uptake while overcoming kinetic and diffusion constraints?

In an attempt to address these questions, the priorities of the laboratory for the ensuing year shall include the following tasks:

- Corroborate via multi-laboratory testing the hydrogen uptake results presently observed for PdHg/CF.
- Conduct in situ Raman and Fourier transform infrared analyses on Pt/AC/BC/IRMOF-8 and PdHg/CF under isothermal hydrogen sorption conditions to elucidate what hydrogenation products are formed in the nano-structured substrates.
- LTDMS experiments will be undertaken to further characterize hydrogen binding sites in Pt/AX-21 and PdHg/CF.
- Examine the catalytic properties of clusters of metallic binary compounds using the LTDMS technique and determine the influence of low-frequency surface plasmon resonances on hydrogen binding and dissociation.
- Prepare new structural motifs for hydrogen spillover based on the intercalation of binary metal compounds in MOFs and evaluate hydrogen sorption properties.
- Conduct *ab initio* and molecular dynamics studies on metal-doped MOF and CF heterostructures to gain additional insights into spillover effects and reconcile experimental observations.

FY 2008 Publications/Presentations

1. M.A. Miller and G.N. Merrill, The Potential Role of Surface Plasmons in Molecular Adsorption and Transformations, 63rd Southwest Regional Meeting of the American Chemical Society, Lubbock, TX, November 4-7, 2007.
2. G.N. Merrill and M.A. Miller, Ab Initio Investigations of Hydrogen Chemisorption on Isorecticular Metal Organic Frameworks, 63rd Southwest Regional Meeting of the American Chemical Society, Lubbock, TX, November 4-7, 2007.
3. M.A. Miller, R.E. Page, and G.N. Merrill, National Testing Laboratory for Solid-State Hydrogen Storage Technologies: Platelet Heterostructures for Solid-State Hydrogen Storage." European Commission's 18-Month Meeting on Novel Efficient Solid-Storage of Hydrogen (NESSHY), Dübendorf, Switzerland, June 18-20, 2007.
4. M.A. Miller and G.N. Merrill, The Role of Low-Frequency Plasmons in Molecular Adsorption: A Theoretical and Spectroscopic Study of Gold and Titanium Compounds." *J. Phys. Chem. C*. 2008, 112, 6939-6946.

References

1. Y.W. Li and R.T. Yang, *J. Am. Chem. Soc.*, 2006, 128, 8136-8137.

2. Y.W. Li and R.T. Yang, *J. Am. Chem. Soc.*, 2006, 128, 12410-12411.
3. M.A. Miller and R.E. Page, FY2007 Annual Progress Report for the Department of Energy Hydrogen Program, available at: [www.hydrogen.energy.gov/annual progress07.html](http://www.hydrogen.energy.gov/annual%20progress07.html).
4. Y.W. Li, F.H. Yang, and R.T. Yang, *J. Phys. Chem. C.*, 2007, 111, 3405-3411.
5. M.A. Miller and G.N. Merrill, *J. Phys. Chem. C.*, 2008, 112, 6939-6946.