

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

- Evaluate and validate the sorption capacity and kinetics of Mg-Li-B-N-H storage materials.

- Evaluate the sorption capacity of Pd-doped polyaniline.
- Further assess hydrogen spillover phenomena in metal-doped carbon foam (CF).
- Assess hydrogen spillover in metal-intercalated metal-organic-framework (IRMOF-16).
- Continue round-robin testing in collaboration with the European Union's hydrogen storage program (Novel Efficient Solid Storage of Hydrogen, NESSHY).

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 the Storage 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 (CoE) 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 the sorption properties of Pd-doped polyaniline (Pd/PANI) at room temperature, using material provided by the University of Nevada, Las Vegas (UNLV), and determined that the maximum uptake at saturation achievable by this material is only 0.8 wt% at 73 bar with fast kinetics (i.e., equilibrium reached within 30 min).
- Using material prepared by University of South Florida (USF), the multi-component complex metal hydride Mg-Li-B-N-H was extensively evaluated to determine capacity, cycle-life, and chemical stability over four isothermal conditions (373-523 K). Experimental measurements showed:
 - maximum reversible uptake of 5.1 wt% at 75 bar, which was observed at highest temperature (523 K).
 - pressure-composition-isotherms were not consistent with those of classical metal hydrides (i.e., equilibrium plateaus were not observed and uptake was shown to increase with temperature).
 - hydride phase formation was kinetically limited.
 - absorption kinetics exhibited an initial steady-state condition within four hours, followed by slow uptake out to 21 hours.
 - material is chemically stable with no detectable quantities of volatile species during desorption.
- In collaboration with the National Center of Scientific Research (NCSR) “Demokritos” in Greece (NESSHY), room-temperature hydrogen spillover effects in PdHg-doped CFs were further investigated for additional batches of material (CF-3, CF-4). Experimental measurements showed:
 - lower hydrogen uptake above 10 bar than previously measured (CF-1), achieving 2.1 wt% at 88 bar for CF-3.
 - evidence of higher degree of unalloyed Pd in the X-ray diffraction (XRD) pattern than in previous batch.

- significant quantity of water is desorbed from PdHg/CF as determined by laser thermal desorption mass spectrometry (LTDMS), likely due to spillover of atomic hydrogen and subsequent binding to oxygen-bearing carbon atoms in CF.
- broad range of stable binding sites for spilt over hydrogen.
- isotopic (D_2) LTDMS confirmed spillover, binding to oxygen and desorption of water (HDO).
- water desorption also detected under high-pressure volumetric conditions.
- By leveraging SwRI®’s parallel research activities, IRMOF-16 compounds entrapping nanoparticles of Ti, TiB_2 , or $AuAl_2$ (i.e., metal intercalated IRMOF-16) were successfully synthesized. These metal-intercalated MOFs adsorbed as much as 1.3 wt% at 80 bar and room temperature for the Ti-IRMOF-16 compound, possibly attributed to hydrogen spillover, and exhibited relatively fast kinetics (14 min for equilibration).



Introduction

Promising classes of materials being developed for reversible on-board hydrogen storage have emerged, thus compelling a rigorous and independent evaluation of their storage capacity, thermodynamics, and kinetics. Occasionally, entirely new chemistries or structural motifs are discovered that yield unexpected properties which must be further studied or validated. Notably, metal organic frameworks (MOFs) [1], destabilized nitrogen-based metal borohydrides [2], and spillover compounds of MOFs and nanoporous carbon materials [3,4], are examples of materials exhibiting surprisingly favorable storage properties which approach the sought-after material targets for on-board storage (Figure 1).

The laboratory has proceeded to evaluate new materials of importance whose validation of hydrogen storage properties is regarded as a high-priority within the solid-state storage community. The most recent priorities for the laboratory have concentrated on evaluating Pd/PANI, Mg-Li-B-N-H complex metal hydride, and PdHg-doped carbon foams (PdHg/CF). In addition to these DOE directives for validation, internally-sponsored materials development activities have been undertaken to synthesize metal-intercalated IRMOF-16 and evaluate whether chemisorptive strategies for hydrogen storage predicated on spillover can be elicited in such structures. These developments were principally motivated by the need to overcome the diffusion-limited kinetics associated with hydrogen

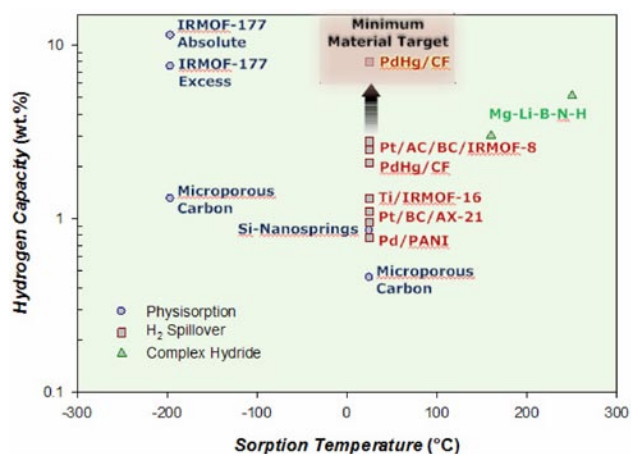


FIGURE 1. The relative performance of physisorption, spillover, and complex hydride materials towards achieving the minimum material target for on-board reversible fuel storage.

spillover effects in surface catalyzed MOF and carbon materials previously studied [3-5].

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 (e.g., the Physisorption CoE), the international community, and SwRI®'s Internal Research & Development Program (IR&D). The laboratory employs a “best practices” approach based on standard operating procedure-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 project provides a venue for the discovery of new materials and the elucidation of unknown mechanisms.

Results

Pd/PANI

The most salient results of our studies over the past year are summarized in Table 1. While only 0.8 wt% uptake was realized at room temperature for Pd/PANI as determined by high-pressure gravimetric analysis, the adsorption and desorption kinetics were both fast, with steady-state conditions typically being achieved under 30 min. Interestingly, an initial conditioning step was required before measureable uptake could be observed. Subsequent sorption cycles demonstrated steep uptake toward saturation at low pressures (<5 bar).

TABLE 1. Overall Summary of Results for Various Classes of Storage Materials Under Investigation

Storage Material	Source	Gravimetric Capacity (wt%)	Comments
Pd/PANI	UNLV	0.8 [298 K, 73 bar]	Fast, reversible kinetics
Mg-Li-B-N-H	USF	5.1 [523 K, 75 bar]	Kinetically-limited phase formation; chemically stable
PdHg/CF	NCSR	2.1 [298 K, 88 bar]	Slow kinetics; evolves water; capacity is sensitive to process variables
Ti-IRMOF-16	SwRI®	1.3 [298 K, 80 bar]	Fast kinetics
TiB ₂ -IRMOF-16	SwRI®	0.2 [317 K, 65 bar]	Thermally activated uptake
AuAl ₂ -IRMOF-16	SwRI®	1.0 [298 K, 65 bar]	Fast kinetics

Mg-Li-B-N-H Complex Hydride

High-pressure volumetric analysis of (Mg-Li-B-N-H), a multi-component composite consisting of three hydrides MgH₂/LiBH₄/LiNH₂ (Mg-Li-B-N-H), showed gravimetric capacities and thermodynamic properties that approach the desired targets for reversible storage. In the present case, the highest reversible capacity was 5.1 wt% at 75 bar and 523 K. Compared with literature data for the individual or binary hydride components, the ternary composite capitalizes on lowered desorption temperatures and abatement of the evolution of ammonia from LiNH₂. Previously reported studies have attributed these properties of the ternary system to a self-catalyzing mechanism in which the products of one reaction nucleate a subsequent reaction [2].

Pressure-composition-isotherms (PCT) for life-cycle experiments carried-out on Mg-Li-B-N-H are shown in Figure 2. In contrast to conventional metal hydrides, plateaus at well defined equilibrium pressures were not readily detected in the PCT curves, which would otherwise be indicative of hydride phase formations. Furthermore, hydrogen absorption is shown in Figure 2 to increase with isothermal temperature. These oddities in the absorption behavior of this ternary composite can be attributed to kinetically-limited phase formation for the conditions under which these measurements were made. Isothermal kinetic profiles measured for absorption and desorption out to 20 h (Figure 3) corroborate the kinetic limitations of phase formation. Desorption at 473 K is relatively fast (<0.05 wt% at 2 h) compared with absorption over the same duration. During absorption, a fast and slow phase is observed, the latter of which shows a steady rise out to 17 h.

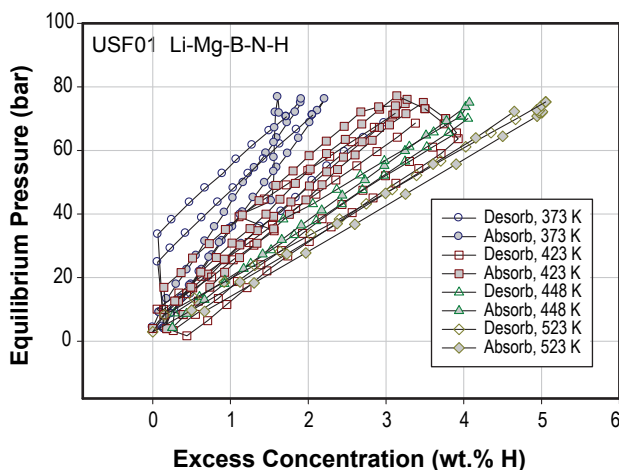


FIGURE 2. PCT curves measured for the ternary complex hydride Li-Mg-B-N-H using high-pressure volumetric analysis.

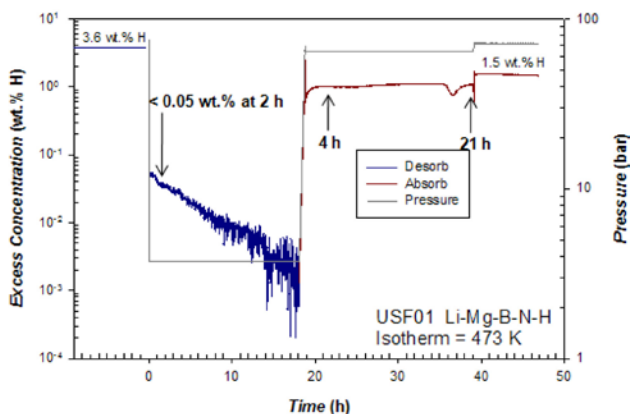


FIGURE 3. Extended Kinetic Profiles Measured at 473 K for Li-Mg-B-N-H

Of particular importance, real-time mass spectrometry measurements performed during PCT life-cycle experiments indicate that volatile species containing boron or nitrogen are not evolved during desorption at 523 K. This result confirms that ternary composites of this kind exhibit chemical stability.

PdHg/CF Spillover Compound

Storage materials predicated on hydrogen spillover effects are under intensive study in our laboratory. In collaboration with NCSR, the storage capacity of PdHg/CF and the spillover mechanism involved was further evaluated in an attempt to validate or reconcile the extraordinary storage capacity (8 wt% at 80 bar and 298 K) reported earlier [6] for the first batch of PdHg/CF (CF-1). Two new batches of CF (CF-3 and CF-4) were synthesized and doped with PdHg nanoparticles for analysis. Prior to volumetric sorption analyses, we attempted to gain additional insights into

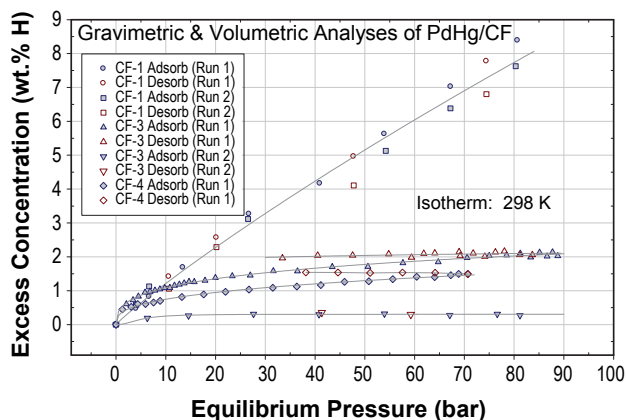


FIGURE 4. High-pressure gravimetric and volumetric sorption isotherms measured for various batches of PdHg/CF at room temperature.

the mechanism of hydrogen uptake by conducting inelastic neutron scattering measurements using the TOSCA instrument at the ISIS synchrotron-spallation neutron source (Rutherford-Appleton Laboratory, UK). These experiments proved to be exceedingly difficult to conduct due to the large background scattering signal from dihydrogen versus that of hydrogen bound to the CF.

The results comparing gravimetric and volumetric analyses at room temperature are shown in Figure 4. Significant differences in the uptake capacity between CF-1 and the new material batches (CF-3 and CF-4) were observed (8 vs. 2.1 wt% at 80 bar). Additionally, the capacity in CF-3 diminished with multiple adsorption cycles. This effect was not observed in CF-1, and led us to believe that the catalytic activity of the PdHg nanoparticles was somehow compromised in CF-3 and CF-4. Upon further characterization of this material, powder XRD measurements showed evidence of alloy segregation into pure Pd and Hg on the CF. It is evident that process variables appear to play a significant role in the measured capacity of these CF-based spillover materials, and further work must be undertaken to resolve these variables.

In order to augment our understanding of the sorption properties and binding energies associated with PdHg/CF, LTDMS measurements were conducted with the goals of determining the number of different “high-energy” binding sites, and assessing whether internal conversion of bound hydrogen to yield water occurs as a side reaction of spillover upon desorption. The latter goal was sought on the premise that carbon foams have been shown to contain a high percentage of oxygen. While such oxygenation of the carbon matrix is thought to be conducive to increasing hydrogen (atomic) binding energies, there is the concern that binding of hydrogen to these sites may internally convert to water molecules upon desorption under certain conditions.

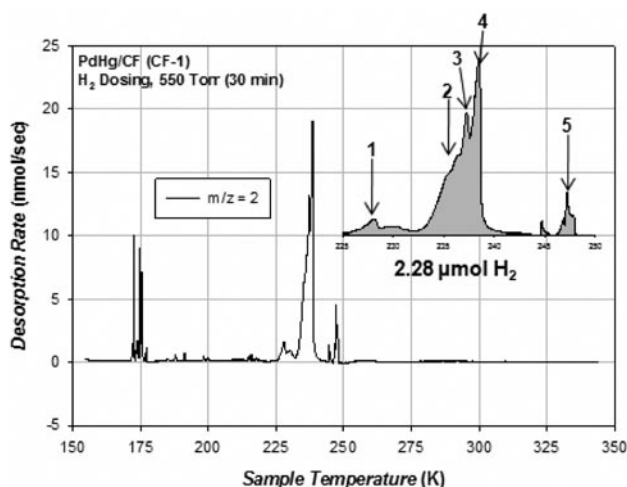


FIGURE 5. LTDSMS profile of hydrogen measured for PdHg/CF, indicating multiple, high-energy binding sites.

In Figure 5, we show a typical result of the LTDSMS desorption profile for PdHg/CF following room temperature dosing of hydrogen. The results indicate that high energy binding sites are indeed present in this material and occur between 225 and 250 K. This energy range is further shown to be substantially above physisorbed hydrogen near 175 K. Expansion of the desorption profile (inset) shows multiple peaks which, after spectral fitting, can be deconvolved into five peaks, each one representing a different type of binding site. The smallest difference in energy resolved for these peaks is 0.3 K.

While the LTDSMS measurements strongly support chemisorptive uptake in PdHg/CF via spillover, we also discovered that water is liberated from this material as a consequence of catalytically-mediated internal conversion of oxygen functional groups in the CF receptor. More elaborate LTDSMS studies linked with deuterium dosings showed that neither D_2 nor HD species were desorbed at detectable levels, but that HDO was desorbed at the same temperature as water. These results indicate that D_2 is dissociated by the PdHg catalyst and is spilled over onto the carbon foam receptor. Atomic deuterium then combines with oxygen-bearing carbons (e.g., -OH) and subsequently desorbs as HDO.

Metal-Intercalated IRMOF-16

A better than present strategy for engineering an “ideal” spillover material was envisaged in which metal clusters are intercalated into a three-dimensional nano-architecture. MOFs are particularly attractive in this regard because the pores of the crystalline framework could potentially lead to entrapment of metal particles or clusters within the framework, thereby forming a network of such particles with long-range periodicity

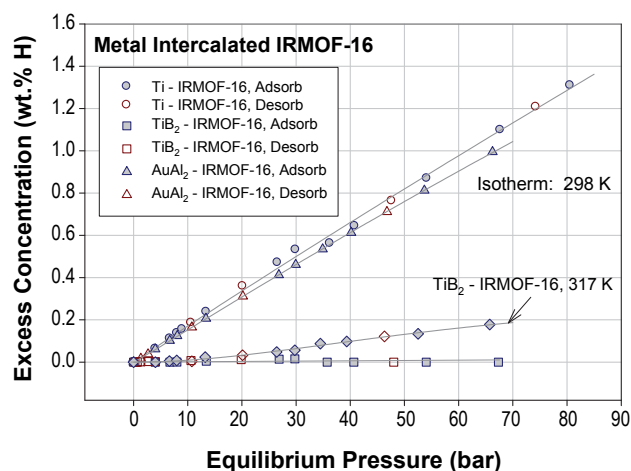


FIGURE 6. High-pressure gravimetric sorption isotherms measured for metal-intercalated IRMOF-16.

and in close proximity to receptor sites for binding of atomic hydrogen. In this pursuit, IRMOF-16 [$Zn_4O(1,4\text{-di}(4\text{-carboxyphenyl)benzene})_3$] compounds entrapping nanoparticles of Ti, TiB_2 , or $AuAl_2$ (i.e., metal intercalated IRMOF-16) were successfully synthesized by in situ entrapment of the metal nanoparticles using an ionic liquid (IL) as a co-solvent. The metal nanoparticles were prepared via direct plasma magnetron sputtering into IL.

In the case of Ti-IRMOF-16 and $AuAl_2$ -IRMOF-16, higher than expected sorption capacities were observed at 298 K (1.2 and 1.3 wt% at 80 bar, respectively). The isotherms shown in Figure 6 are mostly linear, which has been consistent feature of materials exhibiting spillover effects. However, the time required to achieve steady-state conditions at each pressure point was less than 15 min, compared with five hours or more for spillover materials previously investigated [3-5]. Since TiB_2 exhibits a minimum in the density of states at the Fermi level [7], no uptake was observed at 298 K for the intercalated IRMOF-16. At higher temperature (317 K), however, hydrogen uptake, presumably via spillover, could be turned “on” (0.2 wt% at 65 bar), albeit a small amount compared with the Ti- and $AuAl_2$ -IRMOF-16 intercalated compounds.

Conclusions and Future Directions

A renewed interest in complex hydrides can be attributed to the realization that ternary composites of MgH_2 / $LiBH_4$ / $LiNH_2$ exhibit unexpected improvements in thermodynamics, reversibility, and chemical stability. Our measurements indicate that hydride phase formation is significantly limited by kinetics even after this ternary hydride is cyclically conditioned to achieve consistent reversibility. Although this system desorbs hydrogen at lower temperatures than the individual

components, the desorption temperature at which significant quantities of hydrogen can be evolved (523 K) is still too high for practical use. Further improvements in kinetics and thermodynamics are therefore needed.

The potential for chemisorptive strategies via spillover in catalytically-doped nanostructures points to promising opportunities in meeting the DOE on-board storage targets. However, spillover materials have been plagued by exceedingly slow, diffusion-limited uptake and release kinetics. Such diffusion-limited behavior in materials evaluated up to now is principally due to catalyst dispersal being effected by decorating only the surface of a micro- or nanoporous receptor (MOF or carbon). In revisiting metal-doped MOFs as spillover materials, we have shown that entrapping the catalyst in the periodic voids of the framework effectively shortens the diffusion lengths between catalytic centers and a chemisorptive site that lies in close proximity. This arrangement manifests in a dramatic improvement in sorption kinetics that will be explored in other forms of framework compounds.

FY 2009 Publications/Presentations

1. M.A. Miller, C-Y Wang, and G.N. Merrill, "An Experimental and Theoretical Investigation into Hydrogen Storage via Spillover in IRMOF-8," *J. Phys. Chem. C* **2009**, *113*, 3222-3231.
2. L. Wang, F.H. Yang, R.T. Yang, and M.A. Miller, "Effect of Surface Oxygen Groups in Carbons on Hydrogen Storage by Spillover," *Ind. Eng. Chem. Res.* **2009**, *48*, 2920-2926.
3. M.G. Norton, D.N. McIlroy, G. Corti, and M.A. Miller, "Silica Nanosprings – A Novel Nanostructured Material for Hydrogen Storage," *Proceedings of the Clean Technology Conference* **2009**, Houston, TX.
4. Bourlinos, A.; Steriotis, T.; Stubos, A.; Miller, M.A. "Carbon Material for Hydrogen Storage," US Patent Application, Filed November 17, 2008.

References

1. Furukawa, H.; Miller, M.A.; Yaghi, O.M. *J. Mat. Chem.* **2007**, *17*, 3197-3204.
2. Yang, J.; Studik, A.; Siegel, D.J.; Halliday, D.; Drews, A.; Carter, R.O.; Wolverton, C.; Lewis, G.J.; Sachtler, J.W.A.; Low, J.J.; Faheem, S.A.; Lesch, D.A.; Ozolins, V. *Angew. Chem. Int. Ed.* **2008**, *47*, 882-887.
3. Y.W. Li and R.T. Yang, *J. Am. Chem. Soc.*, **2006**, *128*, 8136-8137.
4. Y.W. Li and R.T. Yang, *J. Am. Chem. Soc.*, **2006**, *128*, 12410-12411.
5. M.A. Miller, C-Y Wang, and G.N. Merrill *J. Phys. Chem. C* **2009**, *113*, 3222-3231.
6. M.A. Miller and R.E. Page, FY2008 Annual Progress Report for the Department of Energy Hydrogen Program, available at: www.hydrogen.energy.gov/annual_progress07.html.
7. Miller, M.A. and Merrill, G.N. *J. Phys. Chem. C* **2008**, *112*, 6939-6946.