

IV.F.3 National Testing Laboratory for Solid-State Hydrogen Storage Technologies

Michael A. Miller (Primary Contact)
and Richard A. Page

Southwest Research Institute® (SwRI)
6220 Culebra Road
San Antonio, TX 78238
Phone: (210) 522-2189; 522-3252; Fax: (210) 522-6220
E-mail: mmiller@swri.org; richard.page@swri.org

DOE Technology Development Manager:
Ned Stetson

Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Technical Advisor: George Thomas
Phone: (202) 586-8058
E-mail: George.Thomas@hq.doe.gov

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Ovonic Hydrogen Systems LLC
2983 Waterview Drive
Rochester Hills, MI 48309

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- Assess hydrogen adsorption and spillover phenomena in catalytically-doped carbon-bridged isorecticular MOF (IRMOF)-8 compounds.
- Develop method-based on laser desorption mass spectrometry to evaluate hydrogen binding interactions in spillover compounds.
- Conduct hydrogen charging tests in the full-scale testing facility on a commercial storage vessel (1.8 kg H₂) and subsequently evaluate fire safety performance under a charged condition.

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 Hydrogen Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (F) Codes and Standards
- (K) System Life-Cycle Assessments
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

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.

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 physisorption in metal-organic framework (MOF)-177.

- 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

- Hydrogen low-temperature isotherms were measured for MOF-177 by high-pressure volumetric analysis at 77 K to independently verify hydrogen uptake capacity in this framework compound.
- Room temperature hydrogen isotherms were measured for platinum-doped carbon-bridged IRMOF-8 by high-pressure gravimetric analysis at 298 K to independently validate hydrogen spillover uptake in this activated framework compound.
- Measured and resolved the stable binding sites of hydrogen in IRMOF-8 (Pt/carbon-bridged) spillover compound by laser induced thermal desorption mass spectrometry (LTDMS) to provide mechanistic insight into hydrogen uptake in this compound.
- Utilized the recently completed full-scale test facility to activate and quantitatively charge a prototype vessel containing a proprietary metal hydride for subsequent evaluation of fire safety performance.
- Established round-robin qualification program in partnership with the European Union's (EU's) solid-state hydrogen storage program (Novel Efficient Solid Storage of Hydrogen [NESSHY]) to quantify hydrogen uptake in ultra-microporous carbon and sodium alanate reference materials.



Approach

Upon completing and qualifying a state-of-the-art laboratory facility in 2005, SwRI has proceeded to evaluate materials of major importance which have emerged recently and whose validation of hydrogen uptake is regarded as high-priority within the DOE solid-state storage community. Early in this project, pure and catalytically-doped single wall carbon nanotubes (SWNTs) were given highest priority for evaluation by the laboratory due to the need to resolve confounding data previously reported on the apparent storage capacities of these materials. The results provided by the laboratory helped to guide DOE in focusing research and development efforts on the most promising materials, culminating in a decision not to invest additional resources on pure SWNTs as candidate materials for hydrogen storage [1,2]. However, catalytically-doped SWNTs were shown to exhibit

potentially useful hydrogen binding interactions and, therefore, merited further exploration within the Carbon Center [3].

The most recent priorities for the laboratory have concentrated on verifying hydrogen physisorption uptake in the metal-organic framework MOF-177, $Zn_4O(1,3,5\text{-benzenetribenzoate})_2$, at 77 K and activated hydrogen uptake in platinum-doped carbon-bridged IRMOF-8, $Zn_4O(\text{naphthalenedicarboxylate})$, at 298 K using high-pressure volumetric and gravimetric analyses, respectively. The latter framework compound is hypothesized to undergo activated uptake via spillover of atomic hydrogen into the framework following dissociation of molecular hydrogen at supported metal sites. The transport of atomic hydrogen is thought to be facilitated by the incorporation of carbon-based bridges between the supported metal sites and the framework [4]. Small batches of this compound were synthesized and then provided to the laboratory by two independent groups, University of Michigan and Institute for Nuclear Energy Research (INER) [4], each of whom used similar procedures for their synthesis.

In addition to bulk sorption measurements performed at room temperature for the doped IRMOF-8 compound, laser-induced thermal desorption mass spectrometry (LTDMS) was used to gain additional insights into the existence of specific binding interactions occurring between the carbon-bridged framework and atomic or molecular hydrogen. The high degree of thermal resolution afforded by the LTDMS technique permits one to delineate stable hydrogen binding sites within such composite frameworks that exhibit similar binding energies. These measurements will complement ongoing theoretical studies trying to predict and understand the energies associated with the most probable binding configuration for hydrogen in MOFs and other nano-structured materials.

Results

In earlier work [5], it was reported that the Gibbs excess adsorption for MOF-177 was 7.5 wt% at 70 bar and 77 K. Independent validation of this remarkable result is shown here following high-pressure volumetric analysis at 298 and 77 K. The isotherms for Gibbs excess adsorption are illustrated in Figure 1. These results are in excellent agreement with those reported in the literature, showing in the present case a saturation pressure of 60 bar and a maximum surface excess of 7.5 wt% at 77 K. The adsorption profiles are also consistent with what would be theoretically expected for a microporous material at high pressure, wherein the bulk-gas density exceeds that of the adsorbed gas, thereby showing an adsorption maximum followed by a slight downward decay in the Gibbs excess [6]. The experimental details of this work including a discussion

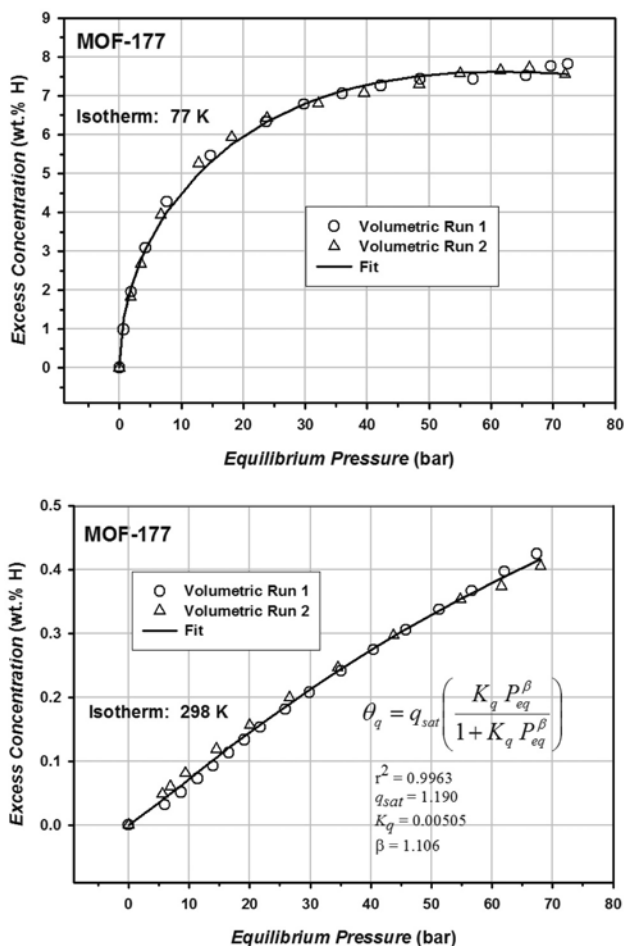


FIGURE 1. High-pressure volumetric sorption isotherms measured for pure MOF-177. Top Panel – Low temperature isotherm (77 K). Bottom Panel – Room temperature isotherm.

on the use of MOF-177 as a benchmark for hydrogen adsorption are described elsewhere [7].

At room temperature, the excess adsorption for MOF-177 is below 0.4 wt% at 60 bar (Figure 1), confirming that the binding interactions for physisorbed molecular hydrogen in non-catalyzed MOFs are much too weak for non-cryogenic storage applications. Alternatively, Yang and coworkers [8] have recently reported that catalytically-doped forms of IRMOF-8 can yield activated uptake at room temperature via hydrogen spillover up to 4 wt% at 100 bar, which is facilitated by incorporating carbon-based bridges within the framework. A characteristic feature of this activated uptake is that the isotherms are linear up to the maximum equilibrium pressure of the analysis (100 bar).

The seminal results of Yang were successfully validated by this laboratory using gravimetric analysis. Figure 2 illustrates the room temperature isotherms for the Gibbs excess adsorption measured from Pt-doped carbon-bridged IRMOF-8 (sample prepared by INER). These results are remarkably similar to those previously

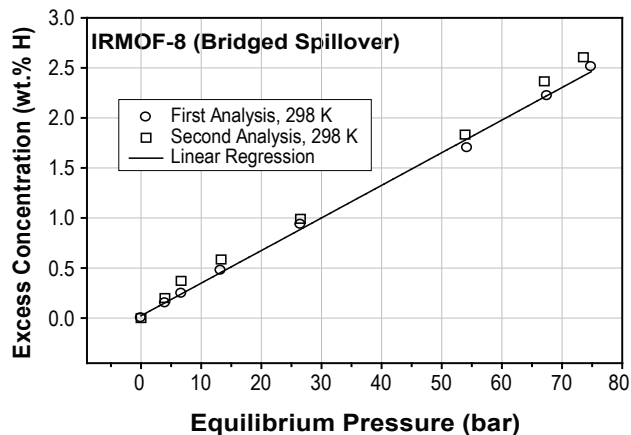


FIGURE 2. High-Pressure Gravimetric Sorption Isotherm Measured for Pt-Doped Carbon-Bridged IRMOF-8 (from INER) at Room Temperature

published [8], confirming linear hydrogen uptake to 2.5 wt% at 75 bar. It is important to note that both laboratories observed exceedingly slow uptake kinetics to the extent that equilibration times for each pressure point in the isotherm was typically greater than five hours. Moreover, these observations are consistent with a hydrogen spillover mechanism as proposed earlier if one considers that the rate-limiting step may be attributed to the migration of atomic hydrogen away from catalytic centers while encountering sufficiently stable binding configurations in the framework.

Additional insights into the nature of specific binding interactions within the doped IRMOF-8 compound (sample prepared by University of Michigan) were gained from the LTDMS spectrum. As illustrated in Figure 3, it is evident from these measurements that multiple binding sites for hydrogen arise in the framework between 263 and 298 K, which are clearly higher in energy than the physisorption peak occurring at 163 K. These results provide the first direct evidence for energetically favorable binding interactions in a doped MOF compound at room temperature.

Conclusions and Future Directions

The principal mission of this laboratory continues to be fulfilled by providing the DOE Centers and outside institutions quantitative validation of the sorption properties of promising new materials for hydrogen storage. As new materials emerge having unique sorption properties, new analytical challenges will also emerge and the techniques needed to accurately quantify these properties will have to be modified or new ones developed. Therefore, it is imperative to this program that not only continuous improvements to the existing methodologies are made, but that advanced new techniques are also developed to probe the mechanistic features of hydrogen uptake in complex structures.

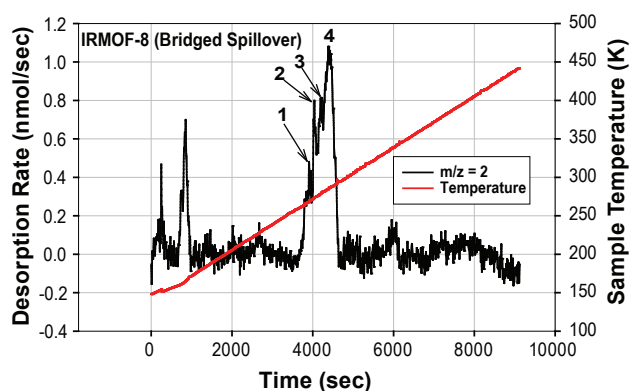


FIGURE 3. LTDMS Profile Measured for Pt-Doped Carbon-Bridged IRMOF-8 (from University of Michigan), Indicating Multiple Occurrences of Stable Binding Sites Between 263 and 298 K

The implementation of LTDMS is an example of this motivation which has proved to be invaluable in confirming and quantifying the occurrence of stable binding sites within doped SWNT and MOF compounds.

Validation of the high physisorption hydrogen capacity in MOFs at low temperatures and the potential for activated spillover at room temperature in doped MOFs points to promising opportunities in meeting the DOE on-board storage targets. Further development of doped framework compounds, such as variations of the doped IRMOF-8 compound recently evaluated, and attainment of a broader than present mechanistic understanding of hydrogen spillover in these compounds should be pursued with urgency. In this light, the priorities of the laboratory for the ensuing year shall include:

- Evaluate additional spillover compounds using gravimetric and volumetric techniques at room temperature, to include Pt-doped carbon-bridged AX-21 (prepared by University of Michigan) and Pt-doped carbon-bridged IRMOF-8 (prepared by INER).
- Perform additional LTDMS measurements on AX-21 and IRMOF-8 spillover compounds.
- Evaluate silicon aerogels by volumetric and gravimetric techniques at 77 K.

- Commence international round-robin testing of ultra-microporous carbon and sodium alanate reference materials in partnership with the EU's NESSHY program.

FY 2007 Publications/Presentations

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2. M.A. Miller, K.E. Coulter and G.N. Merrill, High-Aspect Platelets as Synthetic Platforms for Nano-Engineered Hydrogen Storage Materials, NHA National Hydrogen Conference, San Antonio, TX, March 19-22, 2007.
3. H. Furukawa, M.A. Miller and O.M. Yaghi, Independent Verification of the Saturation Hydrogen Uptake in MOF-177 and Establishment of a Benchmark for Hydrogen Adsorption in Metal-Organic Frameworks, *J. Mater. Chem.*, DOI: 10.1039/b703608f, 2007.

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