IV.E.6 Standardized Testing Program 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
E-mail: mmiller@swri.org; richard.page@swri.org

DOE Managers

HQ: Ned T. Stetson
Phone: (202) 586-9995
E-mail: Ned.Stetson@ee.doe.gov

GO: Jesse Adams
Phone: (720) 356-1421
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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Fiscal Year (FY) 2011 Objectives

Overall

- Support DOE's Hydrogen Storage sub-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.
- Validate the technologies required to achieve the 2015 DOE on-board vehicle hydrogen storage goals.
- Continue new hydrogen storage materials discovery research and development for advanced storage systems.

Current

Analyze hydrogen sorption properties at 77 and 298 K of:

- Polyether ether ether ketone (PEEK)-derived carbon (material provided by the State University of New York, SUNY).
- Microporous carbon (material provided by the National Renewable Energy Laboratory, NREL).
- Porous polymer network (PPN) (material provided by Texas A&M University, TAMU).

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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Verification of Material Performance
  (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
  (A) 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.

FY 2011 Accomplishments

- Validated the hydrogen sorption capacity in PEEK-derived carbon at 77 and 298 K using material provided by SUNY. Experimental measurements showed:
  - Maximum excess concentration of 5.5 wt% at 77 K and 49 bar.
  - Absolute volumetric capacity approaching 38 g/L at 77 K and 71 bar.
- Evaluated the hydrogen sorption capacity in microporous carbon at 77 K using material provided by NREL, which showed 4.8 wt% gravimetric excess adsorption at 45 bar and a volumetric capacity of 28.2 g/L at 70 bar.
- Validated the hydrogen sorption capacity in PPN at 77 and 298 K using material provided by TAMU.

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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] have captured the interest of researchers over the past five years. These examples have resulted in surprisingly favorable storage properties which approach the sought-after material targets for on-board storage (Figure 1).

The laboratory has continued to evaluate important new classes of materials whose validation of hydrogen storage properties is regarded as a high-priority within the solid-state storage community and the DOE. The most recent priorities for the laboratory have concentrated on evaluating hydrogen sorption in PEEK-derived nanoporous carbon and more conventional microporous carbon. A significant amount of experimental and modeling effort was dedicated to the analysis of a PPN based on tetrakis(4-bromophenyl) silane building units [PPN-4(Si)] developed by H-C Zhou's
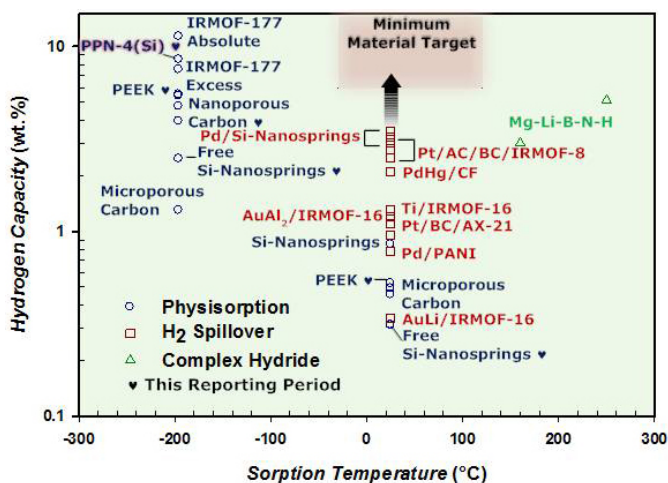
FIGURE 1. Status of material technologies for reversible hydrogen storage via physisorption, spillover, and chemisorption in proximity to DOE material target. New benchmark for excess adsorption is highlighted.

group at TAMU [5]. This material has been shown to exhibit exceptionally-high Brunauer-Emmett-Teller specific surface areas (6,470 m^2/g) with a correspondingly-high gravimetric excess capacity (8.5 wt% at 60 bar) at 77 K: the highest surface area and hydrogen uptake reported to date for a physisorption material.

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 Center of Excellence), the international community, and SwRI's Internal Research & Development (IR&D) program. 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

PEEK-Derived Carbon

The results of our studies over the past year are highlighted in Table 1. In the case of PEEK-derived carbon (as well as other carbon materials), high-pressure volumetric analysis was encumbered by this material's propensity to absorb helium, thus invalidating the use of a helium calibration for determining the skeletal density of the sample (or free volume of the system). To overcome this

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

Material	Source	Surface Excess Amount (wt% H)		Absolute Volumetric Capacity (g/L) 77 K	MOF-177 Benchmark 77 K	
		298 K	77 K		(wt% H)	(g/L)
CO$_2$-Activated PEEK-Derived Carbon	Duke University	0.52 @ 80 bar	5.39 @ 55 bar	30 @ 70 bar	7.5 @ 70 bar	47 @ 70 bar
PEEK-Derived Carbon	SUNY	0.31 @ 81 bar	5.50 @ 49 bar	38 @ 71 bar		
Microporous Carbon	NREL	0.49 @ 80 bar	4.75 @ 45 bar	28 @ 70 bar		
Porous Polymer Network [PPN-4(Si)]	TAMU	0.97 @ 92 bar	8.48 @ 60 bar	28 @ 86 bar		

analytical challenge, the high-pressure gravimetric technique was employed to measure the hydrogen isotherm at room temperature. We then assume in the formal definition of the Gibbs excess that the free energy of the adsorbed fluid is equal to the bulk-gas free energy plus a surface potential term, which we equate to the measured Gibbs excess for the gravimetric mass balance, and thus arrive at a simplified local density (SLD) model. When combined with the Bender equation state to accurately calculate hydrogen gas densities and the gas fugacity, the combined expressions for the SLD model were used in a fitting algorithm to derive the hydrogen skeletal density and the pore volume of the sample by treating these characteristic properties as fitting parameters [6].

The corrected hydrogen isotherms at 77 K measured by the volumetric technique are shown in Figure 2. Here the maximum excess concentration for hydrogen uptake was 5.50 wt% at 49 bar. Using the pore volume derived from the SLD model and fitting algorithm, the profile for absolute volumetric capacity was computed. The absolute volumetric capacity for this material approached 38.2 g/L at 71 bar and, while this is a remarkable result, it falls slightly short of the current benchmark of 40 g/L at 70 bar for MOF-177.

Microporous Carbon

Low-temperature (77 K) hydrogen isotherms were determined using the volumetric technique, again employing the gravimetric technique at room temperature and the SLD model to determine the skeletal density and pore volume of this material. The corrected hydrogen sorption profile, shown in Figure 3, was constructed from four separate analyses due to the long equilibration times associated with each pressure point in the profile. The combined data was fitted to a dose response model in order that the statistical variance of the measurements and the peak excess could be derived. Based on the model fit, a peak uptake for surface excess of 4.75 wt% at 45.3 bar was calculated. The absolute volumetric capacity at 77 K was also determined using the semi-empirically derived pore volume (gravimetric analysis). On this basis, an absolute volumetric capacity of 28 g/L was computed at 69 bar.
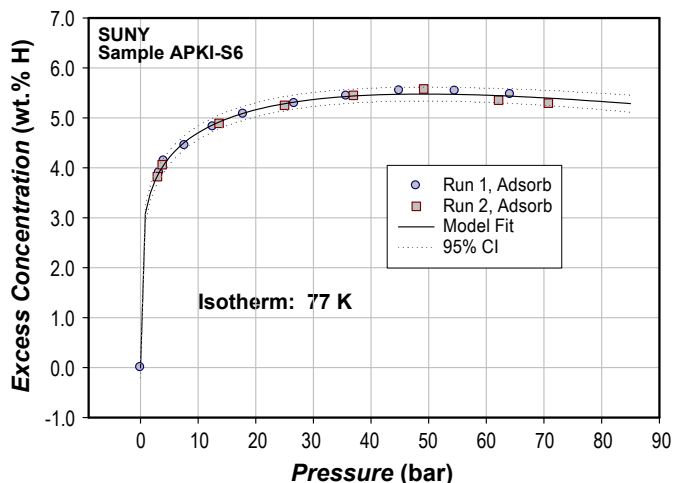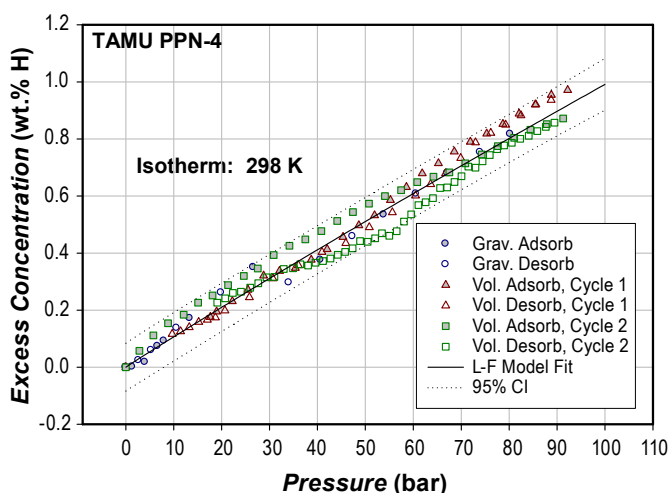

FIGURE 2. Low-temperature (77 K) hydrogen isotherms measured for PEEK-derived nanoporous carbon.
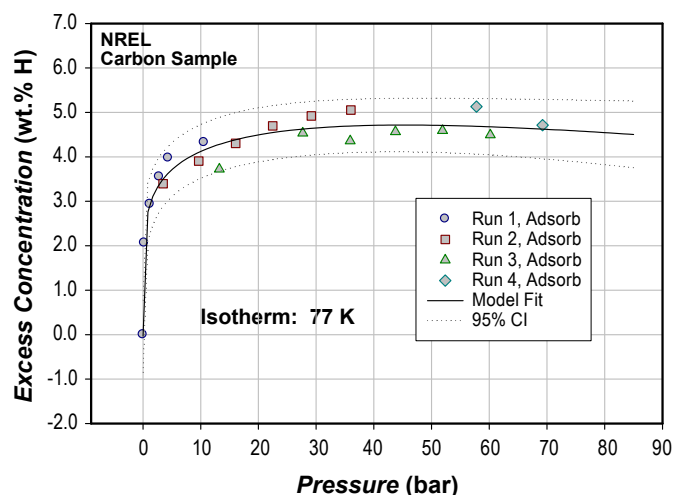
FIGURE 3. Low-temperature (77 K) hydrogen isotherms measured for microporous carbon.

PPN

As in the previous cases for highly active, high surface-area physisorption materials, the analysis of PPN-4(Si) required special attention due to this material's tendency to adsorb helium, thus preventing accurate measurement of the true Gibbs excess concentration and subsequent determination of absolute volumetric capacity. This behavior required that the actual skeletal density be determined using the gravimetric technique. We determined the skeletal density using hydrogen gas and adopted the SLD model as described previously. Additionally, the extremely high specific surface area (6,470 m^2/g) and low bulk density of this material required careful handling methods to prevent fluidization during weighing and sample transfers. These properties further required that the material be mechanically compacted in the sample vessel prior to analysis.

The room temperature gravimetric hydrogen isotherms for the Gibbs excess are compared in Figure 4 with analyses using the volumetric technique at room temperature. The two results are shown to correlate very well after correcting the volumetric measurements for the SLD-derived skeletal density.

The same SLD-derived skeletal density was used to correct low-temperature hydrogen isotherms. After taking into consideration thermal gradient effects, the corrected hydrogen isotherm curves derived from the analyses are represented in Figure 5. In this case, two adsorption and desorption runs (Runs 1 and 2), with thermal-vacuum conditioning between them, were required to construct the composite full-pressure isotherm curves. In order to derive characteristic parameters for the composite data points, a parametric dose-response model was used. The fitted values for the maximum Gibbs-excess concentration at 77 K was 8.4 wt%, which occurred at 60 bar and is higher than our benchmark material, MOF-177 (Table 1).
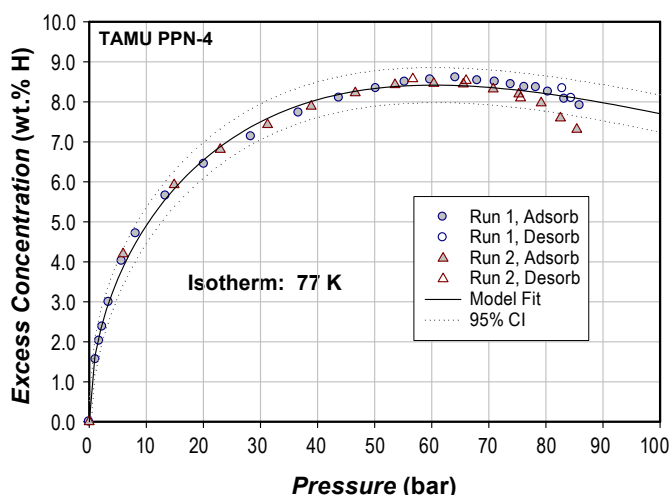
FIGURE 5. Low-temperature (77 K) hydrogen isotherms measured for PPN [PPN-4(Si)] using the volumetric technique.

Additionally, the absolute volumetric capacity was estimated using the SLD-derived skeletal density and adsorbed volume (i.e., pore volume). A value of ~28 g/L absolute volumetric capacity was calculated at 85 bar (77 K). Presently, we have not verified the absolute data theoretically using void-space routines and the kinetic diameter of hydrogen (or helium) since the material is completely amorphous.

Conclusions and Future Directions

In the search for novel forms of active materials for physisorption storage, robust materials have emerged with remarkably high surface areas. Nanoporous carbon derived from PEEK exhibits promising characteristics for hydrogen storage in terms of specific surface area and chemical stability. We found from previous analyses that two forms of such PEEK-derived materials, Duke vs. SUNY, prepared by independent process methods yielded remarkably similar results (Table 1). Additional gains in performance may, however, still be possible as processing methods for the PEEK polymer are further refined.

While the development of new physisorption materials with high surface areas prepared from the pyrolysis of high-melt polymers are promising venues to meeting the much sought-after storage targets, our analyses indicate that engineering the self-assembly of novel classes of non-pyrolytic materials from molecular building units into three-dimensional (amorphous) PPN results in the establishment of a new benchmark in performance for hydrogen excess adsorption: 8.5 wt% at 77 K and 60 bar. An important advantage that PPN structural motifs appear to offer over the existing benchmark, MOF-177, lies in their remarkable thermal and chemical stability, which can be attributed to their entirely covalent bonding network. Indeed, PPNs can be handled in an open-air laboratory environment without

FIGURE 4. Room temperature (298 K) hydrogen isotherms measured for PPN [PPN-4(Si)] using both the volumetric and gravimetric techniques.

impacting their performance. Studies in the future should examine post-synthetic methods of improving the volumetric capacity of these materials, which currently falls short of the MOF-177 benchmark, by examining what effects high-pressure mechanical compaction (i.e., pelletizing) may have on the gravimetric and volumetric capacity of PPN.

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