

## IV.I.1 Standardized Testing Program for Solid-State Hydrogen Storage Technologies

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- Evaluate and validate hydrogen sorption capacity in polyether ether ether ketone (PEEK)-derived carbon material.
- Assess hydrogen spillover effects and kinetics in AuAl<sub>2</sub>- and AuLi-intercalated isoreticular metal organic framework (IRMOF)-16.

### 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 Fuel Cell 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

### 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.

#### Current

- Evaluate and validate the effects of piezo-induced charge on the sorption capacity of nano-porous carbon.

### 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 the effect of piezo-induced charge on hydrogen adsorption in nanoporous carbon at 77 and 298 K, using materials provided by Michigan Tech University, and observed that piezo-induced charge accumulation did not lead to a measureable increase in hydrogen uptake via hydrogen-charge binding interactions.
- Validated the hydrogen sorption capacity in PEEK-derived carbon at 77 and 298 K using material provided by Duke University. Experimental measurements showed:
  - Maximum excess concentration of 5.4 wt% at 77 K and 55 bar.
  - Absolute volumetric capacity approaching 30 g/L at 77 K and 70 bar.
- By leveraging SwRI's parallel research activities, IRMOF-16 compounds entrapping nanoparticles of AuAl<sub>2</sub> and AuLi (i.e., metal intercalated IRMOF-16) were successfully synthesized and characterized. Experimental measurements showed:
  - Excess concentration of 1.1 wt% at 80 bar and room temperature for the AuAl<sub>2</sub>-IRMOF-16 compound, which can be attributed to hydrogen spillover, with relatively fast kinetics (15 min for equilibration).
  - Total loading of intercalated AuAl<sub>2</sub> in IRMOF-16 sample was only 0.13 wt%.
  - Total loading of intercalated Ti in previously-reported Ti-IRMOF-16 compound (showing 1.3 wt% uptake at room temperature and 80 bar) was only 0.04 wt%.



### Introduction

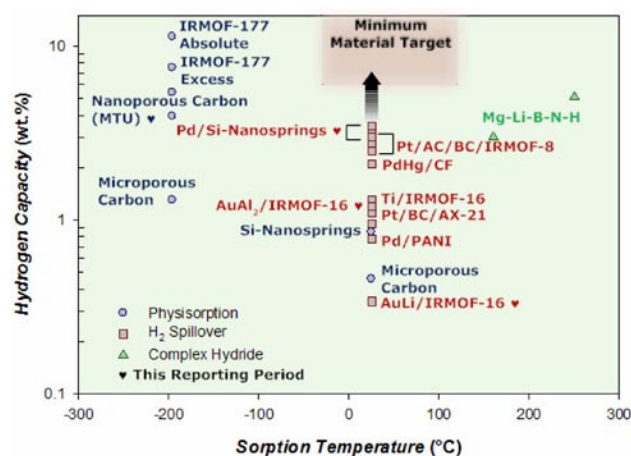
Promising classes of materials being developed for reversible on-board hydrogen storage have emerged, thus compelling a rigorous and independent evaluation of their storage capacity, thermodynamics, and kinetics. Occasionally, entirely new chemistries or structural motifs are discovered that yield unexpected 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, nanoporous carbon materials [3,4], and silica nanosprings, 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 and the DOE. The most recent priorities for the laboratory have concentrated on evaluating piezo-induced charging effects on hydrogen binding interactions in nanoporous carbon, and hydrogen sorption in PEEK-derived nanoporous carbon. In addition to these DOE directives for validation, internally-sponsored materials development activities have been undertaken to evaluate whether chemisorptive strategies for hydrogen storage predicated on spillover can be elicited in AuAl<sub>2</sub>- and AuLi-intercalated IRMOF-16 compounds. These efforts were principally motivated by the need to overcome the diffusion-limited kinetics associated with hydrogen spillover 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 Center of Excellence), 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



**FIGURE 1.** Status of material technologies for reversible hydrogen storage via physisorption, spillover, and chemisorption in proximity to DOE material target.

the program provides a venue for the discovery of new materials and the elucidation of unknown mechanisms.

## Results

### Effects of Piezo-Induced Excess Charge on Hydrogen Binding

The results of our studies over the past year are highlighted in Table 1. An important directive this year was to independently determine whether or not hydrogen uptake could be enhanced by injecting excess charge into a conductive, porous sorbent, such as nanoporous carbon, and thereby provide the means by which the binding energy between dihydrogen and the localized charge on the sorbent could be increased. This idea, which was conceived at Michigan Technological University (MTU) [6], required that we design and construct a highly-modified sample vessel for low-temperature (77 K) sorption measurements. In this modified vessel, the sample was electrically isolated from the assembly via a thin-walled glass insert, while two piezoelectric elements of the lead magnesium niobate-lead titanate type were embedded in the sample at a fixed distance from each other. One pole (i.e., face) of each piezoelectric element was also electrically insulated so that the face of the conductive pole could emit a local excess-charge into the surrounding carbon sample as hydrogen gas pressure was increased.

While the premise of this concept would seem intuitively sound, our laboratory failed to demonstrate a measurable difference in hydrogen uptake between piezo-induced charge generation in nanoporous carbon and the same carbon sample in the uncharged state under identical analytical conditions of the volumetric technique (Table 1 and Figure 2). This difference between hydrogen-charge binding interactions in the charged and uncharged states, however, may have been so subtle due to the experimental conditions employed, such as a low ratio of total charge to sorbent surface area, that the desired effect could not be effectively

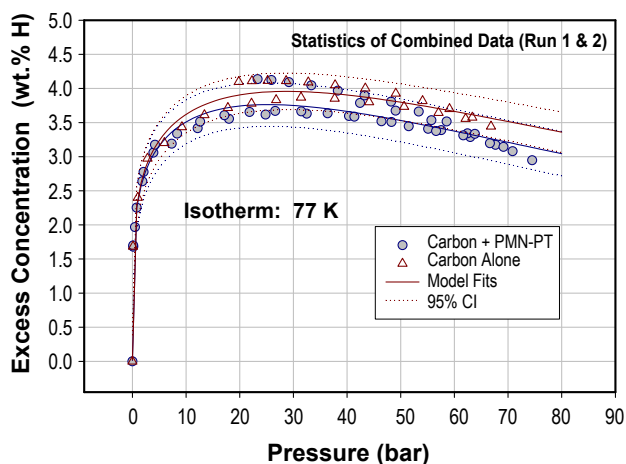


FIGURE 2. Low-temperature (77 K) hydrogen isotherms measured for nanoporous carbon, comparing the effect of piezoelectrically-induced charge generation with the uncharged state.

realized. Indeed, other passive or active modalities of injecting excess charge into a conductive sorbent may be more effective in enhancing hydrogen uptake or increasing the sorption temperature, or both.

### PEEK-Derived Carbon

High-pressure volumetric analysis of PEEK-derived carbon 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 analytical challenge, the high-pressure gravimetric technique was employed to measure the hydrogen isotherm at room temperature. In this case, the simplified local density (SLD) model combined with the Bender equation of state 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 [7].

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

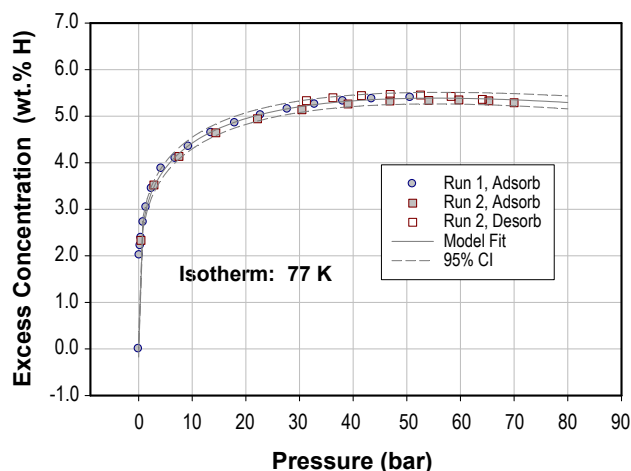
| Storage Material                               | Source     | Gravimetric Excess and/or Absolute Volumetric Capacity (Conditions) | Comments  |
|--|------------|---|---|
| Piezoelectric Transducer/<br>Nanoporous Carbon | MTU        | 3.84 wt% (77 K, 29 bar)   | Piezo-induced excess charge accumulation did not lead to measurable increase in hydrogen uptake compared with carbon alone. |
| Nanoporous Carbon                              | MTU        | 3.94 wt% (77 K, 24 bar)   |   |
| PEEK-Derived Carbon                            | Duke Univ. | 5.39 wt.% (77 K, 55 bar)<br>29.4 g/L (77 K, 70 bar)                 | Relatively fast kinetics, achieving steady-state within ~20 min.  |
| AuAl <sub>2</sub> -IRMOF-16                    | SwRI       | 1.10 wt% (298 K, 80 bar)  | Fast spillover kinetics (~15 min steady-state); only 0.13 wt% catalyst loading.   |
| AuLi-IRMOF-16                                  | SwRI       | 0.30 wt% (298 K, 67 bar)  | Fast spillover kinetics (~15 min steady-state); only 0.10 wt% catalyst loading.   |

LTDMS = laser induced thermal desorption mass spectrometry

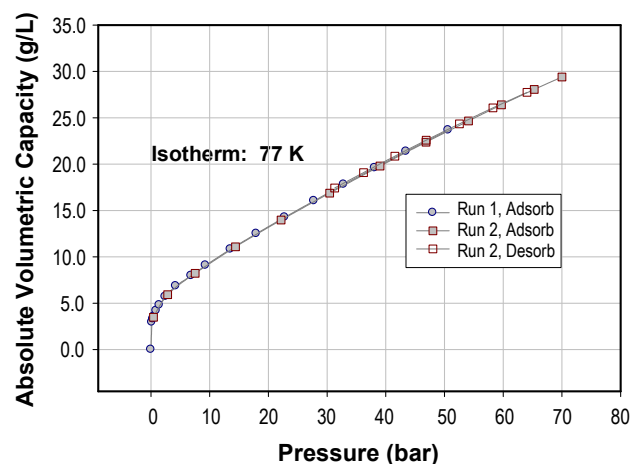
The corrected hydrogen isotherms at 77 K measured by the volumetric technique are shown in Figure 3. Here the maximum excess concentration for hydrogen uptake was 5.39 wt% at 55 bar with no measureable hysteresis in the desorption path. Using the pore volume derived from the SLD model and fitting algorithm, the profile for absolute volumetric capacity was computed as shown in Figure 4. The absolute volumetric capacity for this material approached 30 g/L at 70 bar and, while this is a remarkable result, it is less than the current benchmark of 40 g/L at 70 bar for MOF-177.

### Metal-Intercalated IRMOF-16

Storage materials predicated on hydrogen spillover effects are under intensive study in our laboratory. However, spillover materials exhibiting enhanced



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



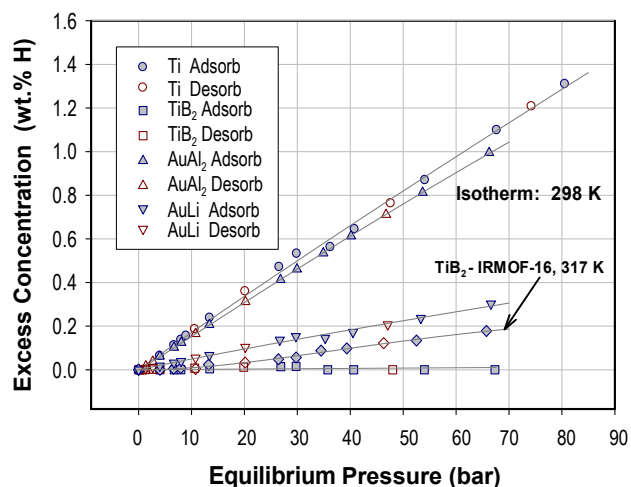
**FIGURE 4.** Low-temperature (77 K) volumetric capacity (absolute) calculated for PEEK-derived carbon.

uptake at room temperature have been consistently plagued by exceedingly slow kinetics, principally because doping of these materials with a catalyst (and bridging compounds) has been limited to the surface of the porous receptor (e.g., carbon or MOF) [3-5]. A better than present strategy for engineering an “ideal” spillover material has been envisaged in which metal clusters are intercalated into (or rather encapsulated by) 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 and in close proximity to receptor sites for binding of atomic hydrogen following catalytic dissociation.

In pursuit of unique spillover motifs with improved kinetics, we have expanded our work on the synthesis and characterization of IRMOF-16 [ $Zn_4O(1,4\text{-di}(4\text{-carboxyphenyl)benzene})_3$ ] compounds entrapping nanoparticles of metal catalysts (i.e., metal intercalated IRMOF-16) by preparing the AuLi-IRMOF-16 and AuAl<sub>2</sub>-IRMOF-16 intercalated compounds [8]. These were successfully synthesized using an ionic liquid (IL) as a co-solvent and in situ entrapment of the catalyst particles. The catalyst compounds used here were previously prepared in our laboratory by depositing each metal alloy into IL *in vacuo* under conditions of plasma magnetron sputtering. In each case, the gravimetric technique was employed to measure hydrogen isotherms at room temperature. The catalyst loading in each compound was also quantified using inductively coupled plasma mass spectrometry (ICP-MS).

The AuAl<sub>2</sub>-IRMOF-16 intercalated compound demonstrated higher than expected hydrogen uptake at room temperature (1.1 wt% excess at 80 bar) (Figure 5), achieving steady-state conditions at each pressure point within 15 min (as compared with 600 min for surface-catalyzed spillover materials evaluated in our laboratory). Surprisingly, the AuLi-IRMOF-16 compound yielded only 0.3 wt% excess at 67 bar. In both cases, however, hydrogen uptake via spillover occurred with only 0.1 wt% loading of catalyst in the voids of the MOF as determined by the ICP-MS analysis.

Overall, we have demonstrated that structural motifs of this kind can dramatically improve the kinetics associated with hydrogen spillover effects by encapsulating catalyst particles within framework voids and distributed therein throughout the bulk framework. This close proximity of catalytic centers to the structural moieties of the receptor shortens the diffusion length associated with the transport of atomic hydrogen to chemisorptive binding sites on the receptor following dissociative spillover.



**FIGURE 5.** Room temperature (298 K) hydrogen isotherms measured for metal-intercalated IRMOF-16.

## Conclusions and Future Directions

The passive (or active) injection of excess charge into a nanoporous carbon is in principle an attractive means of increasing physisorption binding interactions of dihydrogen for enhanced storage, which is deserving of exploration. However, our laboratory has failed thus far to observe experimentally meaningful differences in hydrogen uptake between carbon samples in contact with half-insulated piezoelectric elements for charge generation and the same material in its uncharged state. The lack of supporting results notwithstanding, future work in this area should first seek to calculate the ratio of the total charge theoretically generated by piezoelectric elements (or other means) to the surface area of the carbon material. Such rudimentary calculations would provide the information needed to effectively scale the experimental setup so that differences in hydrogen uptake between the charged- and uncharged states, if they occur, are most likely to fall within the known limits of detection of the sorption technique.

In the search for novel forms and sources of active carbon 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 observed excess gravimetric and absolute volumetric

capacities at 77 K that are approximately 70% of those values for the current benchmark, MOF-177 [1]. Further gains in performance are possible as processing methods for the source PEEK polymer are refined.

The potential for chemisorptive strategies via spillover in catalytically-doped nanostructures points to promising opportunities in meeting the DOE on-board storage targets. In expanding our work on 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 chemisorptive sites that lie in close proximity. As was intended, this arrangement manifests in a dramatic improvement in sorption kinetics at room temperature. Future work should concentrate on refining the structural purity of these sorts of structural motifs so that additional gains in room temperature uptake can be realized.

## FY 2010 Publications/Presentations

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