IV.F.1 National Testing Laboratory for Solid-State Hydrogen Storage Technologies

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2983 Waterview Drive
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Objectives

Overall

- Develop and operate a national-level testing and core reference laboratory aimed at assessing and validating the performance of emerging solid-state hydrogen storage materials and full-scale systems.
- Establish and validate measurement techniques for hydrogen sorption and related performance metrics.

Current

- Qualify laboratory based on outcome of double-blind round-robin testing.
- Assist NREL in independent analysis of single-wall nanotube (SWNT) materials.
- Improve and refine measurement techniques to accommodate most any structure of matter, thermal condition, and sample quantity.
- Complete testing laboratory for full-scale hydrogen storage systems.

Technical Barriers

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

- Standardization of methods suitable to a wide variety of material compositions.
- Development and implementation of standard measurement techniques.

Moreover, this program 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:

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance
(K) System Life-Cycle Assessments
(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. Once fully qualified under the purview of the DOE, the laboratory will play a central role in the down-selection of materials and systems that emerge from the Centers of Excellence and other storage developers by:

- Providing in-depth analysis and understanding of hydrogen physisorption and chemisorption mechanistic behavior.
- Determining and validating material and system storage capacities.
- Providing support in 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.

Accomplishments

- Completed the development and validated the performance of a laser thermal desorption mass spectrometer system for highly sensitive quantitative analysis of very small sample quantities (<50 mg). This system is capable of resolving the relative energies associated with different physisorbed or chemisorbed hydrogen binding sites, which is important in understanding hydrogen sorption mechanistic behavior.
- Completed the installation, modification, and validation of a high-pressure volumetric analyzer for full-pressure sorption isotherm and kinetics measurements over a broad temperature range (77–800 K). This commercial system (PCTPro-2000, Hy-Energy LLC, Fremont, CA) was specially modified to extend its vacuum capability and to include real-time mass spectrometry. Significant effort also went into optimizing the design of its sample vessel for better sample compactness and consistent thermal diffusivity.
- Completed the installation, modification, and validation of a high-pressure gravimetric analyzer for full-pressure sorption isotherm and kinetic measurements. This system was built into a glove box to accommodate handling of air and moisture sensitive samples, and was further modified to include real-time mass spectrometry.
- Gained detailed understanding of important factors affecting the accuracy and precision of low-temperature physisorption measurements.
- Refined technique and apparatus for low-temperature volumetric measurements by examining the relationship between critical point effects and free volume. Low-temperature isotherm results were consistent with those of outside participant labs.
- Demonstrated excellent complementarity between volumetric and gravimetric measurements at 298 K.
- Demonstrated capability of measuring very small sample quantities (< 10 mg) by laser thermal desorption mass spectrometry. The hydrogen capacity of metal-doped SWNTs was measured (2.78 + - 0.19 wt.%), which validated results previously determined at NREL.
- Completed the construction of a dedicated facility for evaluating full-scale storage systems. This facility will address sorption/desorption performance of complete systems up to 5 kg H_2 capacity, refueling time, resistance to exogenous contaminants, and specific energy contained, among other factors related to system durability (e.g., impact, vibration, and fire resistance).

Introduction

The potential for solid-state materials to most efficiently meet the hydrogen storage capacities required to achieve greater than 300-mile range in a fuel-cell powered vehicle has led to significant interest among academic institutions, government-sponsored research facilities, and the commercial sector to accelerate further development of materials and complete containment systems for the storage and delivery of hydrogen at low pressures and at practical temperatures. Promising classes of materials currently being developed for reversible hydrogen storage include catalyzed forms of chemical hydrides, carbon nanostructures and, more recently, sub-nanostructured metal complex grids and metal organic framework (MOF) compounds [1,2]. It is also evident that the discovery of new material structures is occurring at a rapid pace.

The reported storage capacities of these advanced materials have not emerged without controversy, however, and in many instances has been the focus of considerable scrutiny among the scientific community [3-5]. Despite numerous laboratories working on the development of similar materials, the analytical techniques and protocols employed have varied considerably. Consequently, the measurement results have varied to the extent that the potential viability of emerging materials has been difficult to assess. This problem has led to a widespread need to establish a capability to accurately and independently assess the sorption behavior of the wide array of solid-state storage materials employing qualified methods, and focus efforts on those materials that show the most promise. To that end, the U.S. Department of Energy (DOE) has selected Southwest Research Institute®(SwRI) to develop and operate a national-level research and testing facility to evaluate materials and complete systems that may be used to store hydrogen, and to focus national efforts on those that show the most promise. This facility will include a standard testing and certification program to assess the performance of promising solid-state hydrogen storage materials and complete systems. Working with industry, academia, and the U.S. government, the Institute has developed an accepted set of evaluation standards and has begun to evaluate new materials according to those standards.

Approach

In considering the analytical methodologies conventionally practiced for hydrogen sorption measurements, the most suitable technique has been a topic of considerable debate. There are, in general, at least four measurement principles from which to choose: 1) volumetric analysis (Sievert-type apparatus), 2) temperature programmed thermal desorption mass spectrometry (TPD), 3) gravimetric analysis, and,

4) microcalorimetry. A sizeable body of literature has been amassed on each of these techniques over the past several decades for a broad spectrum of different materials. While the merits of each measurement principle can be argued, the complementarity among these choices can be demonstrated as long as the constraint boundaries, such as mass, volume, and thermal stability, are not ignored.

SwRI has completed construction of a state-of-the-art laboratory facility that will establish the standard in the measurement and study of solid-state hydrogen storage technologies. The analytical capabilities of the laboratory facility are distributed around an ultra-high purity hydrogen and helium manifold that include existing as well as new SwRI-developed technologies for highly sensitive quantitative measurements of hydrogen adsorption and desorption under precise thermodynamic control. The overall approach toward completing the facility is illustrated in Figure 1.

The laboratory must ensure that the performance criteria of every element of its activities conforms to the highest standards and achieves the most precise, sensitive, and accurate measurements in characterizing hydrogen storage materials and systems for the DOE, academia, and industry. To ensure that these goals are properly achieved, the laboratory facility is being qualified for official operation by the DOE through a round-robin testing program in collaboration with several other participant laboratories. In this qualification program, at least two different classes of materials (carbon nanostructures and metal hydrides) have been, or will be, distributed to the participant laboratories by the study coordinator where then the sorption capacities are independently determined at two or more isothermal conditions over a broad pressure regime according to that laboratory's accepted methods (Figure 1). At the conclusion of the qualification program, the study coordinator will compile the results submitted by each participant laboratory so that inter-laboratory variances can be assessed. A determination will be made whether SwRI's results fall within an acceptable band of the aggregate variances.

Results

The three central analytical capabilities for hydrogen sorption (Gibbs excess) measurements illustrated in Figure 2 – gravimetry, monometry, and laser desorption mass spectrometry – have been fully implemented into the laboratory facility and have been validated according to prescribed standard protocols developed under this project. A significant amount of effort was dedicated to

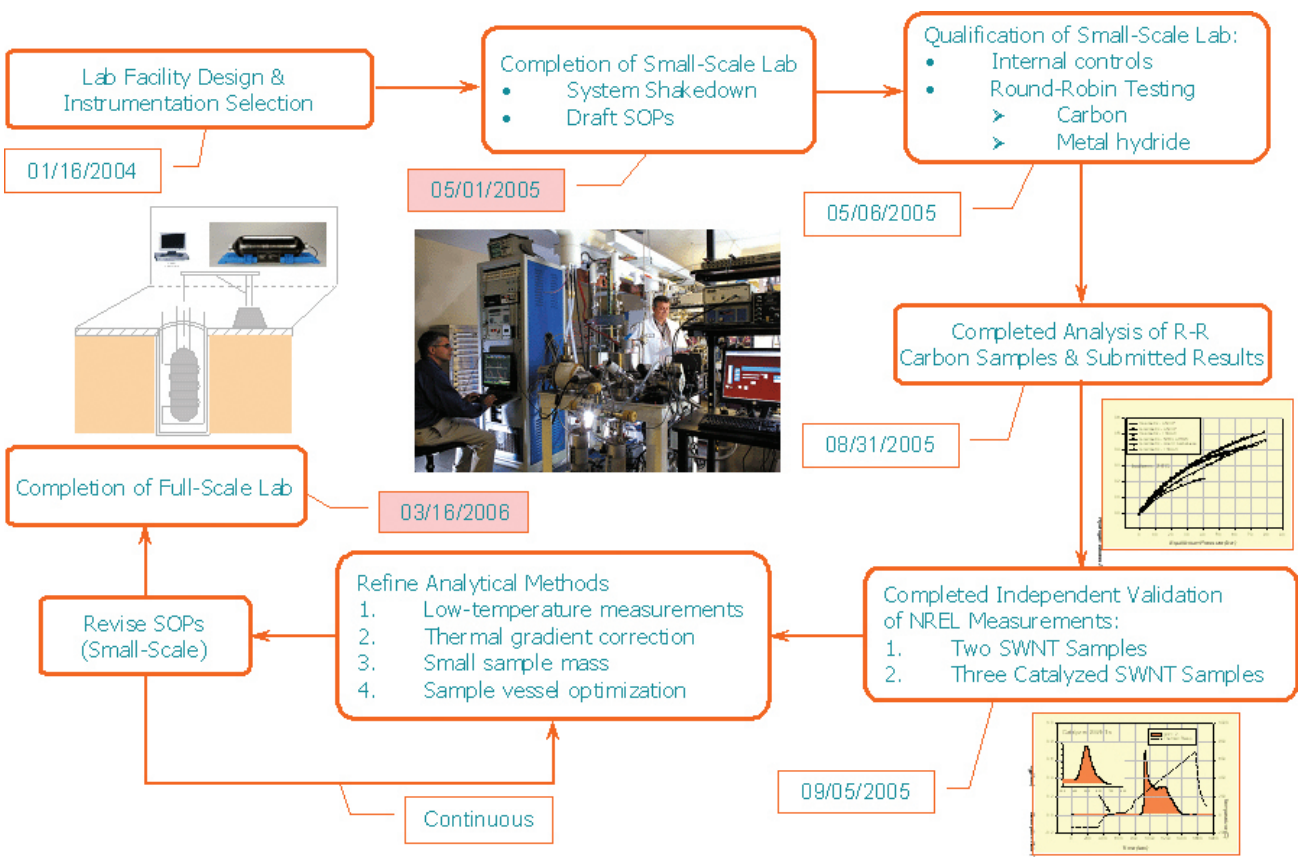


FIGURE 1. Program Plan Sequence and Approach to National Laboratory Qualification

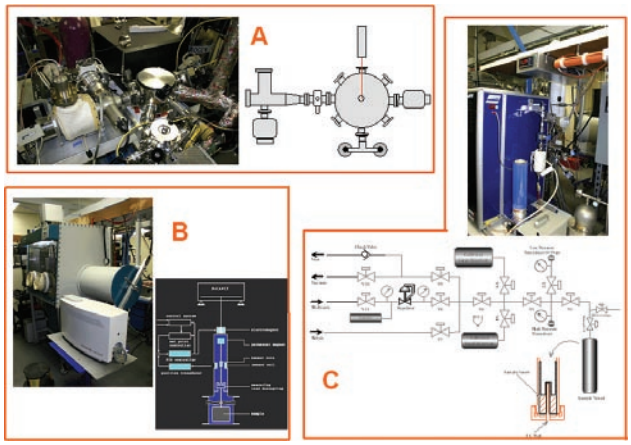


FIGURE 2. Analytical capabilities for hydrogen sorption measurements: (A) laser thermal desorption mass spectrometry (B) high-pressure thermogravimetric analysis linked with mass spectrometry (C) high-pressure volumetric analysis linked with mass spectrometry.

refining both hardware and procedures to accommodate small sample weights and improve accuracy and precision in the measurements over temperature regimes important to gaining a quantitative and mechanistic understanding of physisorption and chemisorption hydrogen uptake. In particular, nano-structured materials that undergo physisorption, such as SWNTs and MOFs, can present several analytical challenges relative to accuracy and precision when attempting to quantify hydrogen uptake at low temperatures (77 K) using high-pressure volumetric analysis (monometry).

Two important goals toward the design of a high quality volumetric sorption experiment at low temperature are to minimize the ratio of the free volume to the sample volume, and to minimize fluctuations in the thermal gradients that arise in the free gas space of the system. It was found that as a consequence of near-critical-point effects, small thermal perturbations in the free-volume gas space from the external system cause uninhibited fluctuations of volume or density in the system [6], which are reflected as pressure fluctuations by the pressure transducers of the instrument. Therefore, in the particularly sensitive phase region near the critical point, it is important to reduce this ratio to such an extent that the susceptibility of the free volume to density fluctuations is significantly limited, and the consequent pressure fluctuations fall below the resolution of the transducers. Related to these effects, the degree of compaction of the sample was also found to be an important factor in achieving sorption isotherms consistent with what would be theoretically predicted. Hence, special consideration was given to optimizing the configuration of the sample vessel and the manipulation of the sample itself so that these effects are minimized in low temperature volumetric analysis, and so reproducible, accurate results can be derived from measurement of nano-structured materials.

Measurement of the Gibbs excess of adsorption for nano-structured materials at high pressures using static thermogravimetric analysis (gravimetry) is principally challenged by suitable methods for correcting the buoyancy of the sample in a dense gas. Compensating this effect by calibrating the system with helium can be problematic for samples of very high surface area as they tend to adsorb helium. Three buoyancy correction techniques were therefore refined to accommodate the unique requirements of measuring hydrogen sorption in nano-structured materials. These techniques have different levels of sophistication depending on whether helium can be used as a calibration gas: (1) a simple equation of state (SEOS), which employs helium as a calibration gas, (2) reference material correction, which uses an inert material (e.g., pure Si) and hydrogen gas, and, (3) the Bender equation of state (BEOS), which uses a highly refined form of the Bender equation to calculate the bulk density of hydrogen over a very broad pressure and temperature regime [7].

Overall, excellent complementarity was demonstrated between the volumetric and gravimetric techniques at room temperature as illustrated for carbon nano-structured materials in Figure 3. At low temperatures (77 K), the refined volumetric method yielded adsorption profiles consistent with what would be theoretically expected at high pressure, wherein

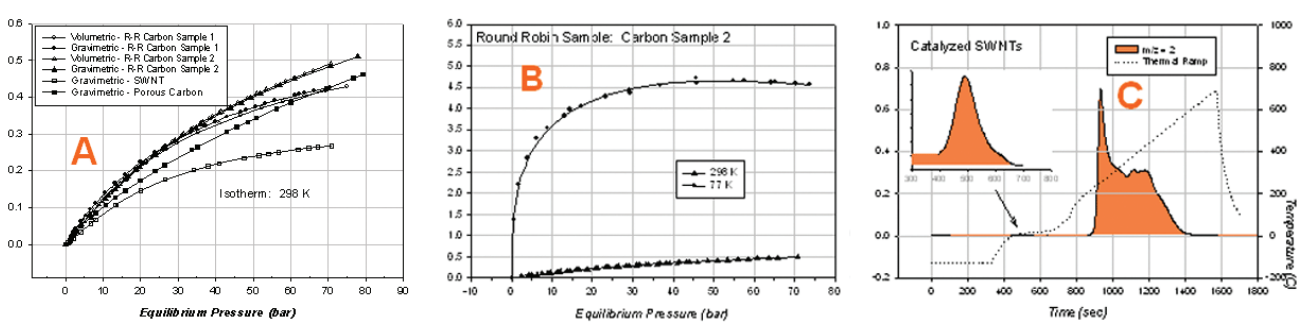


FIGURE 3. Results of sorption analysis for carbon nano-structured materials: (A) room temperature isotherms showing complementarity between volumetric and gravimetric techniques (B) comparison between low-temperature (77 K) and room temperature volumetric measurements (C) thermal desorption mass spectrometry of alloy-doped SWNTs showing low temperature physisorption binding and high temperature binding sites for hydrogen.

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 [8].

The ability to measure hydrogen content in very small amounts of sample (< 10 mg) was demonstrated for alloy-doped SWNTs (synthesized at NREL) using thermal desorption mass spectrometry (Figure 3). The measured hydrogen capacity (2.78 + - 0.19 wt.%) was consistent with previously published data, which provided a clear validation of both the method and published results for nano-structured materials of this form heretofore unsubstantiated by independent analysis [9].

Conclusions and Future Directions

It is evident that the analytical requirements for making accurate and precise measurements of hydrogen sorption are quite rigorous, and the variables associated with the synthesis and preparations of materials suitable for study are convoluted. Therefore, the potential for drawing erroneous conclusions from experiment is very high unless careful steps are taken to ensure that the analytical methodologies employed provide sufficient precision and accuracy, and in particular, that the variables inherent in the processing of materials are clearly understood. At the level of a complete storage system the potential for error in assessing performance is further compounded by the complexity and thermodynamic limit of the engineered system.

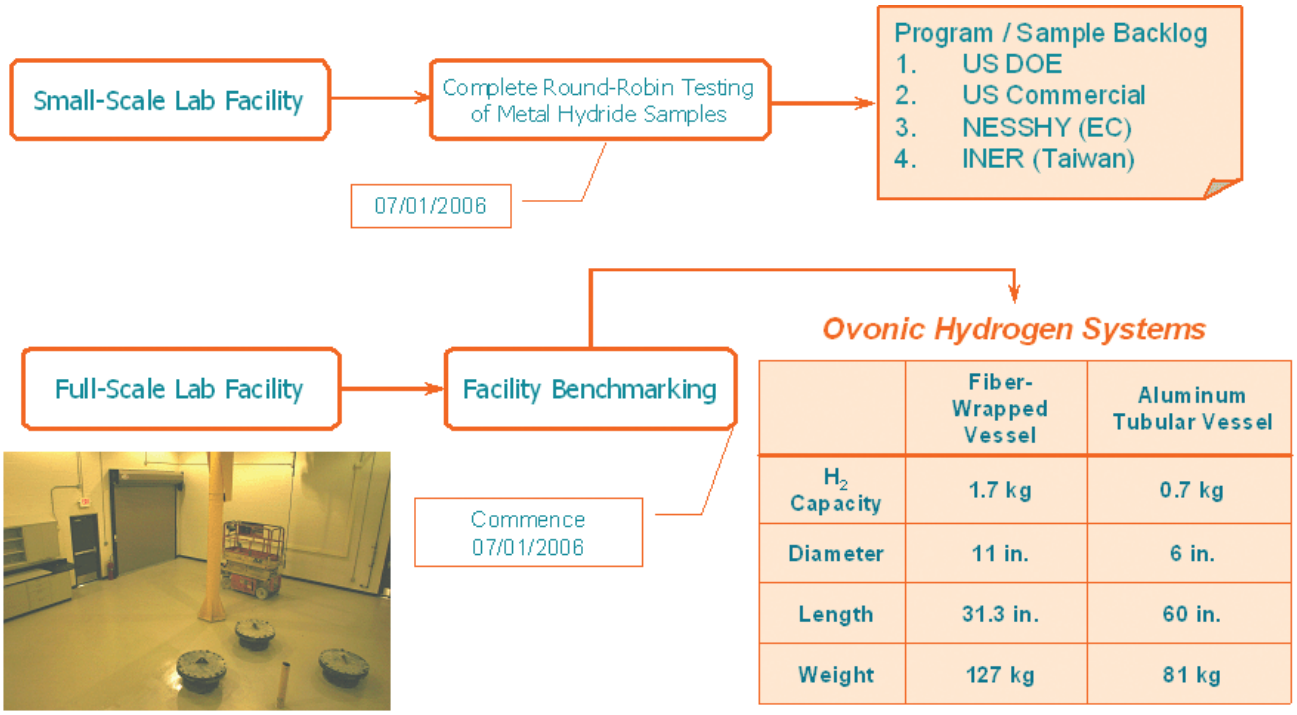
To ensure that the present national-level laboratory facility can meet the analytical requirements expected of the hydrogen storage community, it is imperative that the analytical capabilities of the laboratory are further qualified by extending the round-robin testing program to include other materials and, in particular, complex metal hydrides. This goal will be the focus of activities in the near term so that the demands of the current samples to be tested can be addressed quickly (Figure 4). Test protocols will also be published online. Additionally, having recently completed the full-scale testing facility, its capabilities and analytical methods will be benchmarked using full-scale storage systems provided by Ovonic Hydrogen Systems.

FY 2006 Publications/Presentations

1. M.A. Miller and R.A. Page, National Testing Laboratory for Solid-State Hydrogen Storage Technologies, NHA National Hydrogen Conference, Washington, DC, March 29 –April 1, 2005.

2. M.A. Miller and N. Sridhar, Measurement and Prediction of Material Performance Subject to Hydrogen Exposure, Hydrogen Gas Embrittlement Workshop, ASTM T.G. 01.06.08, ASTM Meeting, Reno, NV, May 17, 2005.

3. M.A. Miller, Development and Application of Standard Methods for Quantifying Hydrogen Sorption in Nanostructured Materials, 2005 Taiwan Symposium on Hydrogen Storage in CNMs, Institute of Nuclear Energy Research (INER), Taipai, Taiwan, Oct. 18-19, 2005.



	Fiber-Wrapped Vessel	Aluminum Tubular Vessel
H_2 Capacity	1.7 kg	0.7 kg
Diameter	11 in.	6 in.
Length	31.3 in.	60 in.
Weight	127 kg	81 kg

FIGURE 4. Near-Term Plan for Small-Scale and Full-Scale Laboratories

4. M.A. Miller, Research Interests in the Confluence and Fundamental Mechanisms of Solid-State Hydrogen Sorption, Surface Enhanced Spectroscopy, and Nano-Scale Chemical Architectures, University of Texas at San Antonio, March 20, 2006.

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