

## III.E Testing and Analysis

### III.E.1 Standardized Testing Program for Emergent Chemical Hydride and Carbon Storage Technologies

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

*Southwest Research Institute™*

*P. O. Drawer 28510*

*6220 Culebra Road*

*San Antonio, TX 78228-0510*

*Phone: (210) 522-3252; Fax: (210) 522-6220; E-mail: rpage@swri.org*

*DOE Technology Development Manager: Antonio M. Bouza*

*Phone: (202) 586-4563; Fax: (202) 586-9811; E-mail: Antonio.Bouza@ee.doe.gov*

#### *Subcontractors:*

*The National Hydrogen Association, Washington, D.C.*

*Energy Conversion Devices, Inc., Troy, MI*

#### **Objectives**

- Develop and operate a standard testing and certification program specifically aimed at assessing the performance, safety and life cycle of emergent complex metal hydrides and carbon adsorption/desorption hydrogen storage materials and systems.
- Work with industry and the U.S. government to develop an accepted set of performance and safety evaluation standards.

#### **Technical Barriers**

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Test Protocols and Evaluation Facilities
- M. Hydrogen Capacity and Reversibility
- F. Codes and Standards
- B. Weight and Volume

#### **Approach**

- Task 1: Perform a comprehensive review of the current accepted practices for testing the performance of complex metal hydride and carbon storage media.
- Task 2: Define the equipment and test protocols that will be used in the standardized testing program.
- Task 3: Design and construct the test facilities for characterizing the performance of complex metal hydride and carbon storage media.
- Task 4: Evaluate the operation of the test facility with actual sample materials to verify that all components operate correctly pursuant to the test protocols developed in Task 2.

- Task 5: Analyze emergent complex metal hydride and carbon storage materials in accordance with the protocols established in Task 2.
- Task 6: Work for the adoption of the test protocols developed in this program by a recognized national or international standards organization.

### **Accomplishments**

- Assembled instruments and ancillary equipment for the characterization of small quantities of solid-state hydrogen storage materials.
- Completed construction of the testing facility.
- Initiated test protocol definition.
- Finalized the design of the full-scale storage system test facility.

### **Future Directions**

- Complete facilities for sorption/desorption measurements on small material quantities (2Q, 2004).
- Submit test protocols to DOE (3Q, 2004).
- Verify instruments and protocols with material standards (4Q, 2004).
- Initiate round-robin validation of facility (4Q, 2004).
- Complete construction of facility for testing of full-scale storage systems (4Q, 2004).

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### **Introduction**

The choices of viable hydrogen storage systems at this time are limited to compressed hydrogen gas (CH<sub>2</sub>), cryogenic liquid hydrogen (LH<sub>2</sub>), chemical hydrides, and solid-state materials such as complex metal hydrides and carbon. Each of these enabling storage technologies has specific advantages and disadvantages; the solid-state storage systems may offer advantages in terms of storage capacity and, most importantly, safety.

The realization that storage systems utilizing solid-state storage materials may most efficiently meet the storage capacity and safety requirements of a hydrogen-based infrastructure has led to significant interest and monetary investment to accelerate the development of complete hydrogen adsorption storage systems. However, there are no standard guidelines, dedicated facilities, nor certification programs specifically aimed at testing and assessing the performance, safety and life cycle of these emergent systems. The development of a standardized testing protocol and system will allow DOE to assess and compare the potential performance of the wide array of materials and

systems and focus their efforts on those that show the most promise.

### **Approach**

In anticipation of the availability of many new materials and technologies for hydrogen storage, the purpose of the present effort is to develop an evaluation facility with established evaluation protocols and standards for the testing and assessment of these emergent solid-state storage materials and systems. Upon thorough validation of the experimental apparatuses and associated protocols, the testing facility and the technical staff that supports it will be available as the focal testing center to any prospective innovator of complex metal hydride or carbon hydrogen storage materials or systems.

The facility will be centered around hydrogen sorption/desorption measurements of small quantities of storage materials. These measurements will be performed using a trio of devices, including a magnetically coupled thermogravimetric analyzer (TGA), a Sieverts apparatus and a thermally programmed desorption apparatus. An ability to test

complete full-sized storage systems will also be included. Volumetric and gravimetric techniques will both be available to characterize the performance of the storage systems.

## **Results**

The first phase of the current project involved a review of the current state-of-the-art in measurement equipment and protocol for characterization of hydrogen storage behavior of small quantities of solid-state materials. A review of the pertinent literature and visits to a number of leading laboratories were conducted (General Motors Research, Air Products, National Renewable Energy Laboratory and Sandia National Laboratory were visited). The general findings of this review were used to design the test facility, details of which are provided below.

### *Analytical Equipment*

The storage capacities of solid-state materials are best understood through the use of phase diagrams, which are often constructed from pressure concentration temperature (PCT) measurements. The PCT measurements are isothermal measurements of the equilibrium hydrogen concentration as a function of the surrounding hydrogen pressure. Two methods are in use for the determination of sorption isotherms: a volumetric method using a Sieverts P-V-T (pressure-volume-temperature) system and a gravimetric method that uses a microbalance for determination of weight changes. Both volumetric and gravimetric capabilities are included in the facility. A brief description of each is provided in separate sections that follow.

In addition to the volumetric and gravimetric capabilities, a thermally programmed desorption (TPD) apparatus has also been included. The TPD is in use in a number of laboratories and has been reported by one of the leading single-walled nanotube (SWNT) R&D groups to yield the most accurate measure of SWNT desorption. Inclusion of the TPD allows comparisons of all three primary techniques in one laboratory and provides the ability to reproduce measurements performed at any laboratory using the same technique in use at that



**Figure 1.** High-Pressure TGA

laboratory. Inclusion of the TPD did not involve a major investment of project funds since a Thermal Desorption and Recoiling Mass Spectrometry (TDARMS) system in place at Southwest Research Institute (SwRI) was converted to the TPD for minimal cost. The TPD is described in a subsequent section.

### *High-Pressure TGA*

The high-pressure TGA, shown in Figure 1, is an automated, state-of-the-art gravimetric system. It incorporates a Rubotherm magnetic suspension balance and a mass spectrometer for gas speciation measurements. The sample chamber is located within a glove box for air-sensitive samples, pressures up to 30 atm can be achieved, and temperature control from cryogenic to 350°C is available. The accuracy of the instrument is dependent upon sample mass and system pressure. Accuracy for a 300-mg sample at 1 atm is estimated to be  $3 \times 10^{-4}$  wt.%.

### *Sieverts Apparatus*

A PCT Pro-2000, shown in Figure 2, is available for volumetric sorption/desorption measurements. The PCT Pro-2000 is a fully automated, state-of-the-art Sieverts instrument for measuring gas sorption properties of materials. The instrument is designed for high-precision measurements on small samples. Measurements can be made at pressures between 0.001 and 200 atm and at temperatures up to 400°C.



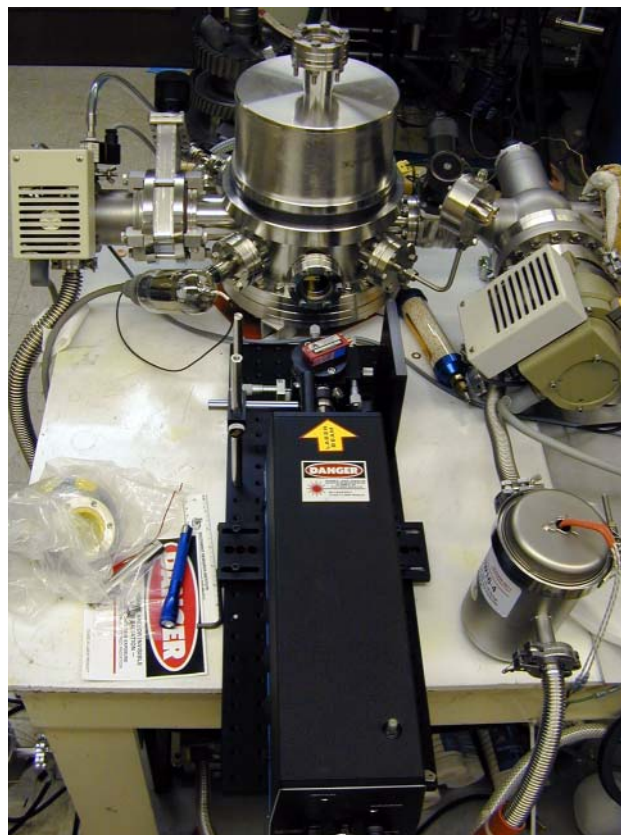
**Figure 2.** Sieverts Apparatus

This instrument has an estimated accuracy of 0.2 wt.% for a 300-mg sample measured at 100 atm.

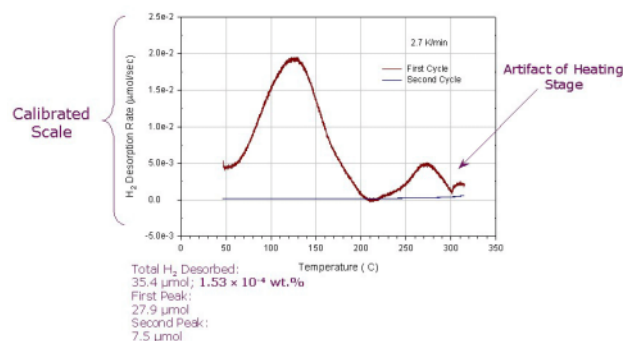
### TPD Apparatus

As the name implies, a TPD instrument is used primarily for hydrogen desorption measurements. It is not effective for generating PCT or kinetic data. Nonetheless, TPDs are in use in a number of laboratories and have produced the highest measures of hydrogen storage capacity for SWNTs. Inclusion of a TPD instrument broadens the capabilities of the facility and allows, along with the TGA and Sieverts instruments, for replication of any measurements made by a material developer.

SwRI had a TDARMS system, which has been converted to a TPD instrument for minimal cost to the project. The SwRI instrument, shown in Figure 3, has a quadrupole mass spectrometer with axial ion source and 90° off-axis secondary electron multiplier detector. It utilizes a high-pressure orifice dual gate-valve interface between the mass spec and the sample chamber. The sample chamber is Summa<sup>®</sup> passivated and evacuated by cryosorption roughing pumps and high-vacuum turbo molecular pumps. To minimize the mass of the heated components within the desorption chamber and provide much more rapid thermal coupling with the sample, laser heating capabilities have been added to the TPD. The laser heating system employs a coated mirror to envelope the sample in the laser beam and an optical modulator to provide control of the photon flux. Hydrogen sensitivity in the  $10^{-6}$  mol range is available with this instrument, as shown in Figure 4.



**Figure 3.** TPD Apparatus



**Figure 4.** Thermal Desorption Results

### Gas Manifold

A gas manifold has been designed that provides a common source of high-purity hydrogen and helium to all of the analytical equipment. The manifold allows pump/purge cleanout with complete bakeout facilities for enhanced removal of adsorbed moisture. Electropolished tubing and valves are used throughout, and the compressed hydrogen and

helium pass through purifiers before entering the manifold and another purifier before entering each test apparatus. Additionally, a mass spec is used to measure gas purity at multiple locations within the manifold.

#### *Storage System Testing*

Characterization of the performance of full-size storage systems will focus on determining their sorption/desorption performance and their refueling rate. To obtain maximum measurement accuracy, the sorption/desorption measurements will be performed at slow rates utilizing volumetric measurement techniques. The refueling time measurements will be performed at rapid fill rates using gravimetric measurement techniques.

#### **Conclusions**

- The testing facility incorporates gravimetric, volumetric and TPD testing capabilities.
- The presence of all three techniques in a single facility should provide higher confidence in results by enabling crosschecks of storage capacity using more than one technique.
- The test protocols and equipment will be verified using material standards followed by a round-robin program.

#### **FY 2004 Publications/Presentations**

1. Project overview presented at FreedomCAR Tech Team Meeting, January 28, 2004, Detroit, MI.
2. Project overview presented at 2004 Hydrogen and Fuel Cells Merit Review Meeting, May 26, 2004, Philadelphia, PA.