

VI.F Testing & Analysis

VI.F.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: Sunita Satyapal

Phone: (202) 586-2336; Fax: (202) 586-9811; E-mail: Sunita.Satyapal@ee.doe.gov

DOE Project Officer: Doug Hooker

Phone: (303) 275-4780; Fax: (303) 275-4743; E-mail: Doug.Hooker@go.doe.gov

Contract Number: DE-FC36-02AL67619

Subcontractors:

The National Hydrogen Association, Washington, D.C.

Energy Conversion Devices, Inc., Troy, MI

Start Date: March 25, 2002

Projected End Date: March 24, 2006

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

Technical Targets

This project is developing laboratory facilities to independently measure the storage capacity of solid state materials and storage systems employing such materials. These facilities will allow DOE to evaluate the wide range of materials that are being developed to meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

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.

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
- Completed shakedown testing of analytical equipment and testing of internal sorption/desorption standards
- Received and initiated sorption/desorption measurements on the first two samples for round-robin verification of the facility
- Finalized the design of the full-scale storage system test facility

Future Directions

- Complete round-robin verification of material testing facility
- Finalize test protocols
- Begin receipt and testing of hydrogen storage materials
- Complete facility for testing full-scale storage systems
- Perform benchmark testing of full-scale storage systems

Introduction

The choices of viable hydrogen storage systems at this time are limited to compressed hydrogen gas (CH₂), cryogenic liquid hydrogen (LH₂), chemical hydrides, and solid-state materials, including complex metal hydrides and carbon. While 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 for assessing the performance of these materials and systems will allow DOE to assess the potential performance of the wide array of materials and systems and focus its 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 this project 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. This included a review of the pertinent literature and visits to a number of leading laboratories. 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 the ability to reproduce measurements performed at any laboratory using the same technique in use at that laboratory. Inclusion of the TPD did not involve a major investment of project funds since a thermal desorption and recoiling mass spectrometry system in place at 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

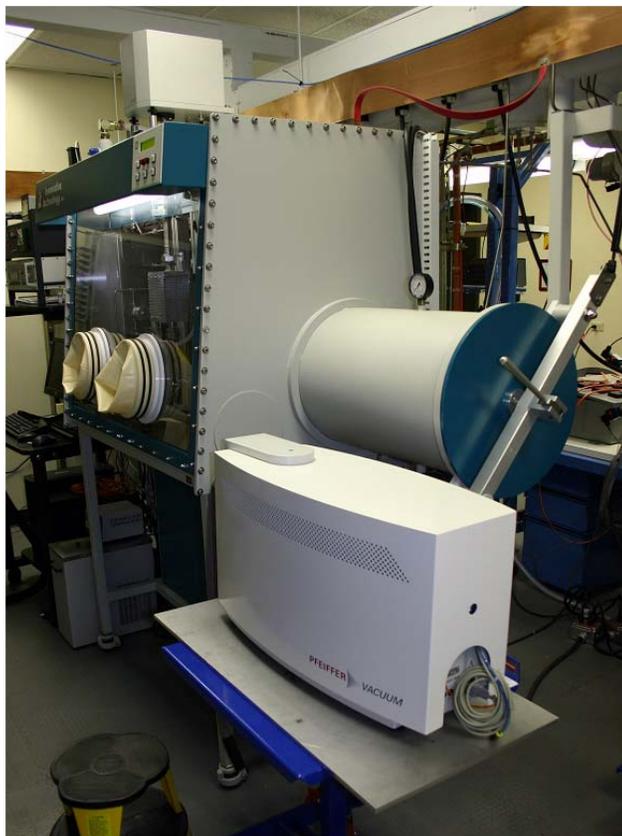


Figure 1. High Pressure TGA with Capillary Mass Spectrometer Interface

dependent upon sample mass and system pressure. Accuracy for a 300 mg sample at 1 atm is estimated to be 3×10^{-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. 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.



Figure 2. Sieverts Apparatus with Capillary Mass Spectrometer Interface

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 TD-ARMS 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[®] passivated and evacuated by cryosorption roughing pumps and high vacuum turbo molecular pumps. To minimize the mass of the heated components

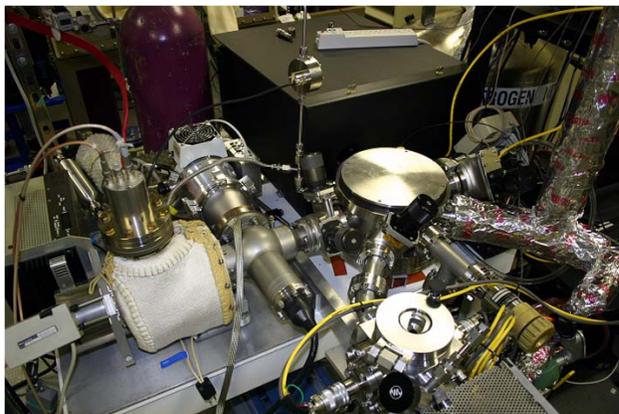


Figure 3. Laser and Photo Thermal Desorption Mass Spectrometer

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.

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 bake-out facilities for enhanced removal of adsorbed moisture. Electro-polished tubing and valves are used throughout and the compressed hydrogen and helium pass through purifiers before entering the manifold and through an additional purifier before entering each test apparatus. Additionally, a fused silica capillary sub-manifold, shown in Figure 4, provides gas for analysis in a mass spectrometer from 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 refueling rates. To obtain maximum measurement accuracy, all measurements will be performed with Coriolis flow meters.



Figure 4. High Purity Gas Manifold with Capillary Fused Silica Gas Sampling Sub-Manifold

Facility Verification

Verification of the analytical instruments for hydrogen storage capacity measurements on small quantities of material is currently underway. Internal verification has been performed using a combination of conventional solid state materials and a National Institute of Standards and Technology (NIST) traceable standard reference material (SRM). A typical desorption profile obtained from the NIST SRM is shown in Figure 5. A blind double round-robin testing program is now underway to provide external verification. Two carbon materials are in hand and currently being tested. At least three metal hydrides are currently being prepared for inclusion in the round-robin program.

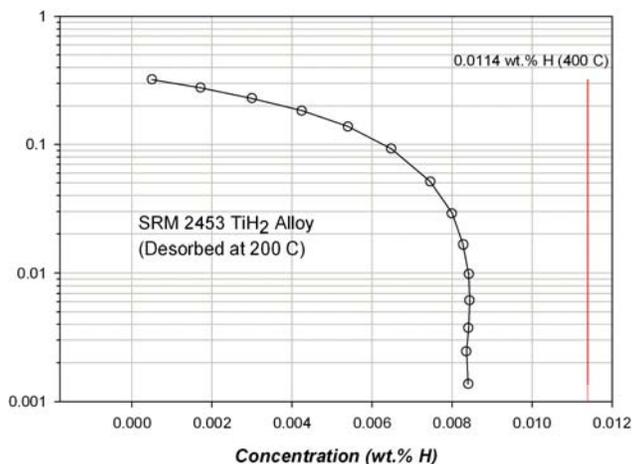


Figure 5. Hydrogen Desorption Result from NIST Standard Reference Material

Summary

- 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 cross checks of storage capacity using more than one technique.
- The test protocols and equipment have been verified using internal material standards.
- A double blind round-robin verification program is currently underway.

FY 2005 Publications/Presentations

1. Project overview presented at Freedom Car Tech Team Meeting, January 28, 2004, Detroit, MI.
2. Project overview presented at 2005 Hydrogen and Fuel Cells Merit Review Meeting, May 25, 2005, Washington, D.C.
3. National Testing Laboratory for Solid State Hydrogen Storage Technologies, NHA Annual Hydrogen Conference, March 30, 2005
4. Project overview presented at Storage Testing and Analysis Workshop, May 26, 2005, Washington, D.C.