

Standardized Testing Program For Emergent Chemical Hydride And Carbon Storage Technologies

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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 R,D&D Plan:

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

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

- Completed literature review of current measurement state-of-the-art.
- Developed preliminary facility and equipment design.
- Completed visits to leading laboratories involved in hydrogen adsorption/desorption measurements.
- Submitted document specifying the equipment to be used for characterization of solid-state hydrogen storage materials.

Future Directions

- A testing facility equipped to perform gravimetric, volumetric and thermally programmed desorption (TPD) measurements on small quantities of solid-state hydrogen storage materials has been defined (2Q, 2003).
- The design of the facility to test full-scale storage systems will be finalized (3Q, 2003).
- Construction of the facility for testing small quantities of solid-state hydrogen storage materials will be completed (2Q,2004).

Introduction

The choices of viable hydrogen storage systems at this time are limited to compressed hydrogen gas (CH₂) storage tanks, cryogenic liquid hydrogen (LH₂) storage tanks, 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, or certification programs specifically aimed at testing and assessing the performance, safety and life cycle of these emergent systems. The development of a standardized protocol and testing system would allow both DOE and the R&D organizations to assess

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. Although the final form of the test protocol and equipment is still being defined, it is anticipated that the test system will be centered around hydrogen sorption/desorption measurements of small quantities of storage materials. These measurements may be performed using a trio of devices, including a magnetically coupled thermogravimetric analyzer (TGA), as shown in Figure 1, a Sieverts apparatus, as

shown in Figure 2, and a thermally programmed desorption apparatus. An ability to test complete storage systems will also be included.

The performance characteristics of candidate materials will be determined through a comprehensive materials characterization and systems testing approach. This approach will encompass the elements described below.

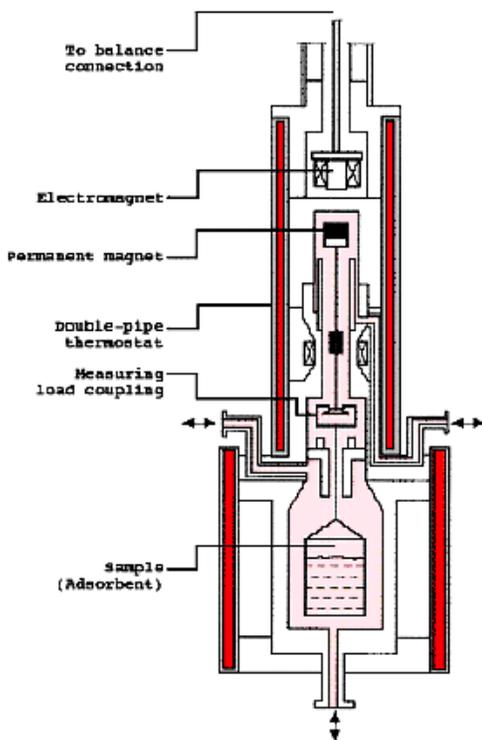


Figure 1. Magnetically Coupled Thermogravimetric Analyzer

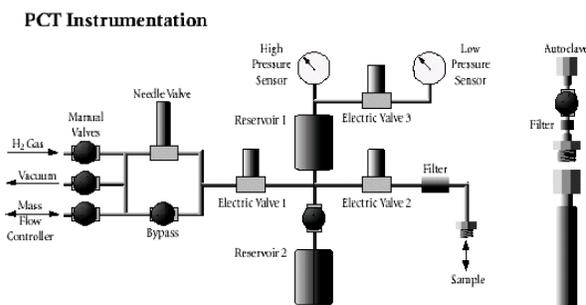


Figure 2. Schematic of Sieverts Apparatus

Certification of Chemical Composition and Crystallographic Properties. Materials selected for evaluation will be analyzed to determine or verify their elemental composition and crystallographic properties using appropriate analytical capabilities: atomic adsorption spectroscopy (AAS), X-ray fluorescence (XRF), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and powder X-ray diffraction.

Evaluation and Certification of Performance Parameters. The intrinsic thermodynamic characteristics of candidate storage materials, where existing data is not available, will be evaluated by modulated differential scanning calorimetry (MDSC). Data of this sort that has already been generated by others will be used to the extent that it is relevant to the specific goals of the present study. The intrinsic thermodynamic characteristics that will be derived from the MDSC analysis include the following:

- Determination of first and second order phase transitions
- Heat of transition
- Transition temperature
- Non-reversible transitions (such as in decomposition)
- Decomposition temperature
- Decomposition exotherm
- Crystalline versus amorphous compositions

Once the intrinsic thermodynamic characteristics are firmly established, the storage materials will be subjected to the performance assessment test protocols. The performance parameters and conditions that will be derived from the testing regime are as follows.

- Specific energy contained in storage system
- Sorption/desorption cycle life
- Resistance to exogenous contaminants
- Average refueling time
- Most favorable thermal-cycle conditions
- Impact resistance (only applicable to complete hydrogen storage container technologies)

- Vibration resistance (only applicable to complete hydrogen storage container technologies)
- Fire resistance (only applicable to complete hydrogen storage container technologies)

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. The review involved a review of the pertinent literature and visits to a number of leading laboratories. Specifically, General Motors Research, Air Products, the National Renewable Energy Laboratory and Sandia National Laboratories were visited. The general findings of the review of the current state-of-the-art are summarized below.

1. The wide range of materials currently under investigation results in a wide range of measurement conditions, e.g., sample quantities ranging from 1 mg to 1g and environments ranging from vacuum to 100 atm.
2. Three prominent techniques are being used to measure hydrogen storage capacity: gravimetric (TGA), volumetric (Sieverts) and thermally programmed desorption (TPD).
3. Errors in measurement results have generally been related to the indirect nature of the techniques (TGA and Sieverts) and/or operating near the sensitivity limits of the equipment.
4. Single walled nanotubes (SWNTs) are currently the most challenging material to measure due to a combination of very small mass and high pressure. However, one laboratory depends on hydrogen desorption measured in a vacuum environment.

Proposed 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. It has been proposed that both volumetric and gravimetric capabilities be included in the facility. A brief description of each is provided in separate sections that follow.

In addition to the volumetric and gravimetric capabilities, the inclusion of a thermally programmed desorption (TPD) apparatus has also been proposed. The TPD is in use in a number of laboratories and has been reported by one of the leading SWNT R&D groups to yield the most accurate measure of SWNT desorption. Inclusion of the TPD will allow comparisons of all three primary techniques in one laboratory and offers the possibility to reproduce measurements performed at any laboratory using the same technique in use at that laboratory. Inclusion of the TPD will not involve a major investment of project funds since a Thermal Desorption and Recoiling Mass Spectrometry (TDARMS) system in place at SwRI can be converted to a TPD for minimal cost. The TDARMS/TPD is described in a subsequent section.

High Pressure TGA. A high pressure TGA has been proposed for the gravimetric measurements. The proposed TGA incorporates a Rubotherm magnetic suspension balance and a mass spectrometer for gas speciation during desorption measurements. The accuracy of the instrument will be 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 . It has been proposed that a PCT Pro-2000 be employed 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. Nonetheless, TPDs are in use in a number of laboratories and have produced the most accurate measures of hydrogen storage capacity for SWNTs. Inclusion of a TPD instrument in the facility would broaden capabilities and allow, along with the TGA and Sieverts instruments, for replication of any measurements made by a material developer.

SwRI has a TDARMS system, which is being converted to a TPD instrument for minimal cost to the project. The SwRI instrument 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 spectrometer and the sample chamber. The sample chamber is Summa[®] passivated and evacuated by cryosorption roughing pumps and high vacuum turbo molecular pumps. The sample stage and heating are being modified for hydrogen desorption measurements.

Conclusions

The following conclusions have been drawn from the results of the review.

1. No single measurement technique will be appropriate for all of the materials that are currently being considered for hydrogen storage.
2. A comprehensive testing facility will need to have multiple techniques to cover the full range of materials.
3. The presence of multiple techniques will provide higher confidence in results by enabling cross checks of storage capacity using more than one technique.
4. Whenever possible, gas speciation should be included in the measurement of storage capacity.

FY 2002 Publications/Presentations

1. Project overview presented at FreedomCAR Tech Team Meeting, September 19, 2002, Detroit, MI.
2. Project overview presented at Sandia National Laboratories, November 18, 2002, Livermore, CA.
3. Project overview presented at IHIG H2 Storage Working Group Meeting, February 13, 2003, Chicago, IL.
4. Project overview presented at 2003 Hydrogen and Fuel Cells Merit Review Meeting, May 20, 2003, Berkeley, CA.