IV.A.3 Best Practices for Characterizing Engineering Properties of Hydrogen Storage Materials

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Project Start Date: February 7, 2007
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- To prepare reference documents detailing best practices and limitations in measuring hydrogen storage and engineering properties of materials.
  - The documents are reviewed by experts in the field.
  - The final documents will be made available to researchers at all levels in the DOE hydrogen storage sub-program.

Fiscal Year (FY) 2013 Objectives

- To complete document section 6: “Measurements of Engineering Thermal Properties of Hydrogen Storage Materials”
- To complete document section 7: “Measurements of Engineering Mechanical Properties of Hydrogen Storage Materials”

Technical Barriers

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

(A) System Weight and Volume
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(J) Thermal Management
(P) Reproducibility of Performance

Technical Targets

The goal of this project is to prepare reference documents detailing the recommended best practices and limitations in making critical performance and engineering properties measurements on hydrogen storage materials. These reference documents will provide a resource to improve the accuracy and efficiency of critical measurements to aid the projects and ultimately the entire program to achieve or exceed the technical storage targets.

In particular this project is focused on the following target-related performance measurements:

- Kinetics: System fill time for 5-kg hydrogen, minimum full-flow rate and start time to full-flow
- Capacity: gravimetric and volumetric capacity
- Thermodynamic Stability: maximum/minimum delivery pressure of H_2 from tank and impact on capacity and kinetic-related targets
- Cycle-Life Properties: cycle life and cycle life variation
- Heat Transfer Properties: system fill time for 5-kg hydrogen, minimum full-flow rate and start time to full-flow

FY 2013 Accomplishments

- Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents.
- External contributions and review of Engineering Thermal Properties section completed through collaborations with:
  - Dr. Maximilian Fichtner, Karlsruher Institute for Technology, Germany
  - Dr. Robert Bowman Jr., Consultant to U.S. Department of Energy
  - Dr. Ewa Rönnebro, Pacific Northwest National Laboratories
  - Dr. Bart van Hassel, United Technologies Research Center, USA
  - Dr. Lars Röntzsch, Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Dresden, Germany
  - Dr. Michel Latroche, Institut de Chimie et des Matériaux de Paris Est CNRS, France
  - Dr. Patricia De Rango, Institut Néel CNRS, Grenoble, France
  - Dr. Mike Veenstra, Dr. Jun Yang, and Dr. Andrea Sudik, Ford Motor Co.
  - Dr. Bruce Hardy, Savannah River National Laboratory
  - Professor David Grant and Dr. Alastair Stuart, of the University of Nottingham, United Kingdom
- Sections 1-5 (Introduction, Kinetics, Capacity, Thermodynamic, and Cycle-Life Properties sections 100% complete.
- "Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials" sections 1-5 posted on DOE website for world-wide access. Please download the current document from: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage.pdf
- Thermal Properties section 6, 100% complete and posted on DOE website for world-wide access. Please download the current document from: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage_section_6.pdf
- Mechanical Properties section currently in progress.

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INTRODUCTION

The Hydrogen Storage sub-program goal is the development of hydrogen storage materials that meet or exceed the DOE's targets for the onboard hydrogen storage in a hydrogen-powered vehicle. The growth of research efforts in this field and new approaches to solving storage issues has brought the talents of a wide-range of researchers to bear in solving the grand challenge of hydrogen storage. There is a need to have common metrics and best practices for measuring the practical hydrogen storage properties of new materials that are being developed within the DOE Hydrogen Storage Program as well as at an international level. H2 Technology Consulting is tasked with creating clear and comprehensive resources that will provide detailed knowledge and recommendations for best practices in the measurements of these properties.

APPROACH

This project is a combined approach of documenting the experience the primary contact and other experts in the field have with these measurement, incorporating examples from the literature, performing experimental measurements to demonstrate important issues, and finally, condensing key information into concise reference guides. Each section covers such topics as the overall purpose of the measurements, some basic theory, experimental consideration, methods of measurement, and many details on both material properties and experimental factors that may strongly influence the final results and conclusions. Participation from other experts in the field is being sought out for input, relevant examples, and critical review at all levels.

RESULTS

This year work was completed on the "Best Practices for Characterizing Engineering Properties of Hydrogen Storage Materials" document section 6 covering the measurement of Thermal Properties of hydrogen storage materials and it is now posted on the DOE website.

For this work collaborations were established with the following international experts in the field: Ewa Rönnebro, Pacific Northwest National Laboratory; Bart van Hassel, United Technologies Research Center; Lars Röntzsch, Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Dresden, Germany; Michel Latroche, Institut de Chimie et des Matériaux de Paris Est CNRS, France; Patricia De Rango, Institut Néel CNRS, Grenoble, France; Mike Veenstra and Jun Yang of Ford Motor Co.; Bruce Hardy, of Savannah River National Laboratory; and David Grant, of the University of Nottingham, United Kingdom. In addition, the work has been coordinated and has received important scientific input through our contract monitor Phil Parilla at the National Renewable Energy Laboratory.

This year's second task is on section 7: Engineering Mechanical Properties measurements. It includes:

1. The examination of benefits and limitations of methods for measuring porosity, skeletal, apparent, and packing densities.
2. The validity of translating measurements on small samples to full systems scale performance.
3. Currently used and alternative methods for measuring material expansion forces will also be presented.

The objective of this subtask is to review measurement techniques currently being used for measuring mechanical properties of hydrogen storage materials. As this has not been done extensively in this field, the task will include an evaluation of common mechanical properties measurement methods used in other applied materials fields that may be appropriate for hydrogen storage materials. A focus will be on clarifying problem areas in these measurements and to establish some common methods.

The following are some examples of the content of the work performed in FY 2013 on these two engineering properties sections.

Section 6: Measurements of Engineering Thermal Properties of Hydrogen Storage Materials

Thermal Conductivity: Thermal conductivity is a property of a conducting medium and, like the viscosity, is primarily a function of temperature [1]. Thermal conductivity *k (*sometimes given by the symbol *λ),* in ($W{\cdot}K^{-1}{\cdot}m^{-1}$), describes the ability of a material to transfer heat. This transfer of heat is defined by Equation 1 (called Fourier's law):

Equation 1

$$Q_x = -kA\frac{\mathrm{d}T}{\mathrm{d}x}$$

where Q_x is the heat transfer rate in the x direction, in W; A is the area normal to direction of heat flux, in m^2; $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient in the x direction, in $K^{-1}{\cdot}m^{-1}$, and k is the thermal conductivity, in $W{\cdot}K^{-1}{\cdot}m^{-1}$. The negative sign indicates that the flux is down the gradient, and it can be shown from irreversible thermodynamics that the coefficient k is always positive.

There are many different methods to measure thermal conductivity and there are a number of considerations in selecting an appropriate measurement method beginning with the form of the material (gas, liquids, solids, powders) and the temperature range for which the material will be used. Section 6 of the Best Practices document describes in detail a wide range of methods and the criteria for selecting the most appropriate technique for hydrogen storage materials measurements. One example is the "Guarded Hot Plate" measurement method. Figure 1 presents a schematic representation of a guarded hot plate instrument for measuring thermal conductivities of powdered hydrogen storage materials.

The Guarded Hot Plate method uses unidirectional heat transfer through a pair of identical samples. A temperature gradient within each sample is formed by producing a known heat flux to a hot plate between the samples while providing a heat sink at a cold plate on the opposite side of each sample. The temperatures at each side of the samples are measured when the system reaches steady state. Using the heat flux, sample thickness and surface areas, and temperature measurements, Fourier's unidirectional heat conduction equation can then be applied to easily calculate an effective thermal conductivity for the samples.

Another example is the in situ measurement of effective thermal conductivity using the Thermal Probe method. The thermal conductivity of sodium-alanates was measured under a variety of charged and discharged condition by Dedrick et al. using the thermal probe method and finite element modeling. The apparatus developed for those measurements is shown in Figure 2.

The accurate determination of the effective thermal conductivity and heat capacity of storage materials, additives, and system components is critical for modeling and design of advanced systems. An example of materials and system modeling is given below for an advanced complex-

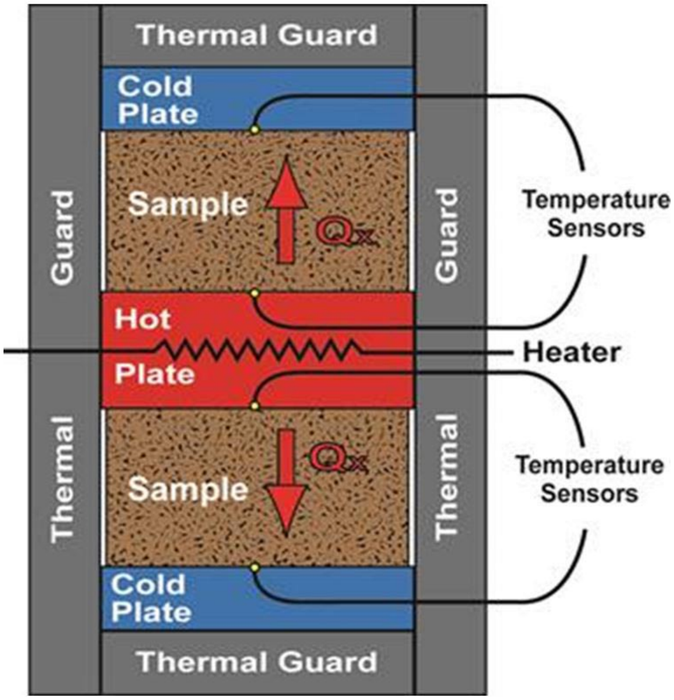

FIGURE 1. Schematic of Basic Guarded Hot Plate Design

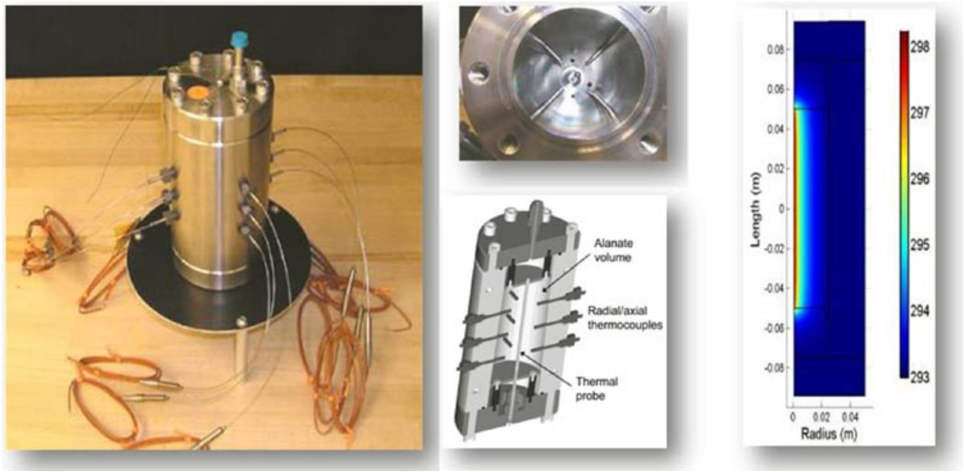

FIGURE 2. Instrumented Chamber and Modeling Results to Measure Thermal Conductivity and Wall Resistance as a Function of Phase, Temperature, Cycle, Morphology, and Pressure [2,3]

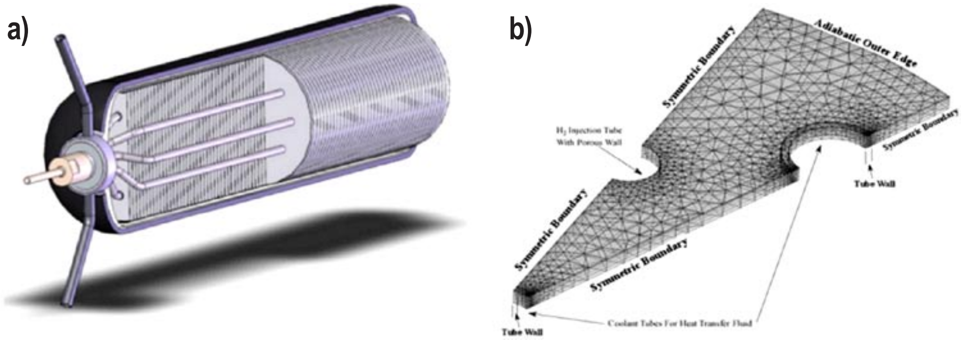

FIGURE 3. a) Example of a Shell, Tube and Fin Complex Hydride Bed Configuration [5]; **b)** Geometry for a Three-Dimensional Shell, Tube and Fin Computations Model [4]

hydride ($TiCl_3$ doped sodium alanate) system that includes a shell and tube heat transfer solution. The low thermal conductivity of the alanate necessitated design features that maintained a relatively short length scale for heat transfer within the bed. A schematic rendition of a prototype system (United Technologies Research Center) and the geometric configuration of the finite element model (Savannah River National Laboratory) are shown in Figure 3. Computational modeling was used to be able to simulate the behavior of complex metal hydride tanks [4].

Simulation results for charging the bed are shown in Figure 4. The image (left) shows the reduction in temperature from the mid-plane of the hydride layer to the mid-plane of the fin. The plan view (right) shows the temperature profile over the mid-plane of the hydride layer. Such modeling aids in understanding and designing for large temperature gradients in complex hydride-based storage beds. A critical requirement is the input of accurately measured parametric data such as the effective thermal conductivity and heat capacity of the storage material and components.

The Section 7: Measurements of Engineering Mechanical Properties of Hydrogen Storage Materials

Lattice volume expansion on hydriding has a significant impact on the mechanical properties of hydride storage materials. Hydrogen absorption causes varying degrees of decrepitation in metal hydrides. Cycling and vibration in normal hydrogen storage applications can cause segregation and interlocking of microscopic particles which, by expansion during hydriding, can impart enormous forces on a containment vessel, change material storage properties, and affect the long-term stability of the storage materials. Figure 5 is a schematic representation of an example of the process and potential impact (material-based mechanical failure of a hydride storage tank) of the mechanical properties of hydrogen storage materials.

Lattice expansion, decrepitation, particle size distribution, and expansion forces are some of the many important mechanical properties of hydrogen storage

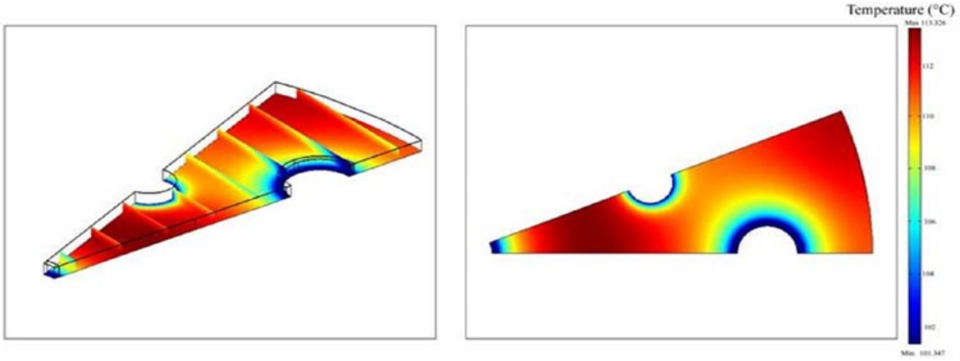

FIGURE 4. Isometric and Plan Views of Temperature Profile for Three-Dimensional Model at 40 Seconds; Base of Isometric Figure is at Bed Mid-Plane (center of the hydride bed layer between fins) [4]

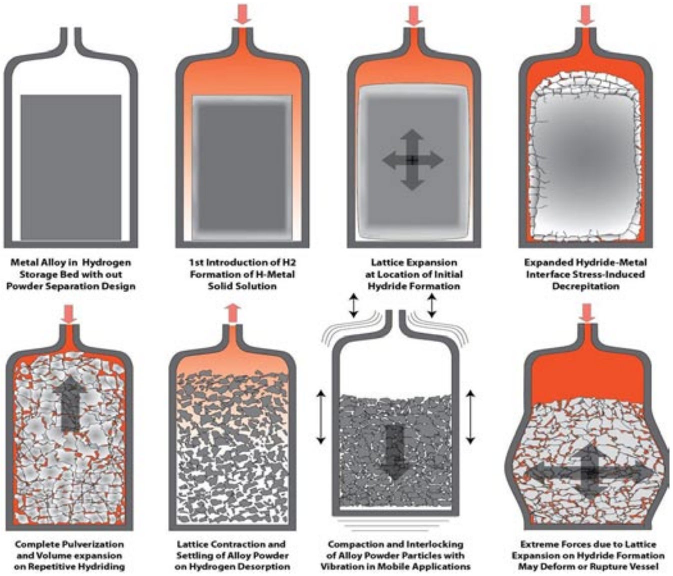

FIGURE 5. Schematic Illustration of Hydride Expansion in Confined Storage Vessel

materials that must be measured and evaluated in the process of developing advanced hydrogen storage systems.

CONCLUSIONS AND FUTURE DIRECTIONS

In FY 2013 we were able to establish important collaborations and technical assistance from experts in the field. We finalized section 6: "Measurements of Engineering Thermal Properties of Hydrogen Storage Materials." in a timely manner. We are currently working on completing the final version of the Engineering Mechanical Properties measurement section (7) of the document.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. "Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials" sections 1-5 posted on DOE website for world-wide access. Please download the current document from: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage.pdf

2. Thermal Properties section 6, 100% complete and posted on DOE website for world-wide access. Please download the current document from: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage_section_6.pdf

SPECIAL RECOGNITIONS & AWARDS

1. 2013 DOE Hydrogen and Fuel Cells Program; Hydrogen Storage Sub-Program Award recognizing outstanding technical contributions
http://www.hydrogen.energy.gov/annual_review13_awards.html

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