

IV.E.2 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

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

Technical Targets

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

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

- Kinetics - targets: system fill time for 5-kg hydrogen, minimum full-flow rate and start time to full-flow
- Capacity - targets: gravimetric and volumetric capacity
- Thermodynamic Stability - targets: maximum/minimum delivery pressure of H₂ from tank and impact on capacity and kinetic related targets
- Cycle-Life Properties - targets: cycle life and cycle life variation
- Heat Transfer Properties - targets: system fill time for 5-kg hydrogen, minimum full-flow rate and start time to full-flow

Fiscal Year (FY) 2012 Objectives

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

Technical Barriers

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

FY 2012 Accomplishments

- Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents.
- External review (U. Nottingham, U.K.) of Thermodynamics section completed.
- All input and edits incorporated into final version of Hydrogen Storage Materials Properties section.
- Final Introduction section 100% complete.
- Final Kinetics section 100% complete.
- Final Capacity section 100% complete.
- Final Thermodynamic section 100% complete.
- Final Cycle-Life Properties section 100% complete.

- Posted final “Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials” sections 1-5 to 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 90% complete.
- Thermal Properties section currently being reviewed by international experts.



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 sub-program as well as at an international level. H2 Technology Consulting is tasked with creating a clear and comprehensive resource 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 a concise reference guide. 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 “Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials” document sections 1-5 covering the measurement of materials related

hydrogen storage properties. The final version including a preface, introduction, kinetics, capacity, cycle-life, and thermodynamics measurement sections is now posted on the DOE website.

This year’s main focus was on the new Engineering Properties document of the Best Practices Project. The first section of this document covers the best practices in making Engineering Thermal Properties measurements. It includes:

- A review of measurement techniques currently being used for measuring thermal conductivity and heat capacity properties of hydrogen storage materials.
- An evaluation of common thermal property measurement methods used in other applied materials fields that are appropriate for hydrogen storage materials.
- Important issues in making the measurements and analyzing the data that contribute to errors in the results.
- The specific need for data to support scale-up system design.
- How the measurement methods need to be tailored for new materials being developed to address heat transfer issues.

For this new work collaborations were established with the following international experts in the field: Ewa Rönnebro, Pacific Northwest National Laboratories; 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., USA; Bruce Hardy, of Savannah River National Laboratory; David Grant, of the University of Nottingham, United Kingdom; and Daniel Dedrick, Sandia National Laboratories. 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.

The objective of this subtask is to review measurement techniques currently being used for measuring thermal properties of hydrogen storage materials. As this has not been done extensively in this field, the task will include an evaluation of common thermal property 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 this new Engineering Thermal Properties section.

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 ($\text{W}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$), describes the ability of a material to transfer heat. This

transfer of heat is defined by Equation 1 (This equation is called Fourier's law):

Equation 1

$$Q_x = -kA \frac{dT}{dx}$$

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 ; dT/dx is the temperature gradient in the x direction, in $K \cdot m^{-1}$, 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.

Multiplied by a temperature difference (in Kelvin, K) and an area (in square meters, m^2), and divided by a thickness (in meters, m), the thermal conductivity predicts the rate of energy loss (in watts, W) through a piece of material. Thermal conductivity and conductance are analogous to electrical conductivity ($A \cdot m^{-1} \cdot V^{-1}$) and electrical conductance ($A \cdot V^{-1}$).

In its most simple form, the measurement of thermal conductivity of a solid involves applying heat to one end of a sample of a uniform shape and measuring Q_x and dT/dx to determine k by means of Equation 1. This is shown diagrammatically in Figure 1.

There are many different methods to measure thermal conductivity. The method selected should be appropriate for the general type of material (gas, liquids, solids, powders) and the temperature range for which the material will be used. Some common measurement methods that are presented in detail in the document are:

- Guarded Hot Plate Method (ASTM C 177)
- Concentric Cylinders Method
- Concentric Spheres Method
- Thermal Probe Method (ASTM D 5334)

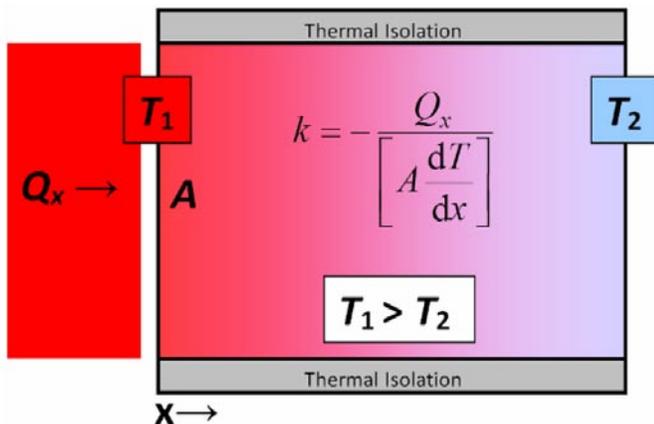


FIGURE 1. Schematic diagram a simple thermal conductivity measurement of a solid

- Transient Plane Source (TPS) Method
- Divided Bar Method (ASTM E1225-87)
- Hot-Wire Method (ASTM C1113) for Gases and Liquids
- Flash Method

Figure 2 illustrates the wide range of thermal conductivities for common materials and shows the generally applicable range of thermal conductivity for common measurement methods. For example, for highly conductive ceramics, metals or diamond composites, the laser flash method is often employed. Whereas, the thermal conductivity of refractory materials is typically determined on large samples using hot wire instruments.

For hydrogen storage systems based on hydrogen storage materials the hydrogen gas itself may play a very important role in the systems' heat transfer. The thermal conductive of several gases as a function of gas pressure are presented in Figure 3 [3]. With the decrease in the pressure, the thermal conductivity of the gas decreases because of the increase in the mean free path of the gas molecules (Smoluchowski effect [4]).

Knowing the thermal conductivity of hydrogen storage materials under operating conditions is important because during charging or hydrogen release the interaction of hydrogen and the storage materials often produces or consumes large amounts of heat. Without sophisticated means of heat transfer, this heat will cause a significant rise in temperature which, among other things, will have a strong impact on hydrogen uptake or delivery rates.

The accurate determination of the effective thermal conductivity and heat capacity of storage materials, additives, and system components is also critical for modeling and design of advanced systems. An example of materials and system modeling is given below for an advanced metal-hydride system that includes an aluminum foam heat transfer solution. A test system as shown in Figure 4 was built and data from those tests were used to validate a numerical model that was developed to be able to simulate the behavior of metal hydride tanks [5].

Simulation results for charging the bed are shown in Figure 5 and compared with measured data.

The flow rate and hydrogen capacity (mass transfer) of the simulations were in relatively good agreement with the experimental results and demonstrated the need for adequate heat transfer. Such modeling relies on accurate values of the thermal properties of the hydrogen storage materials and system components.

Two possible solutions for improving thermal conductivity are 1) to compress the hydrogen storage materials, and 2) to add a second material with high thermal conductivity.

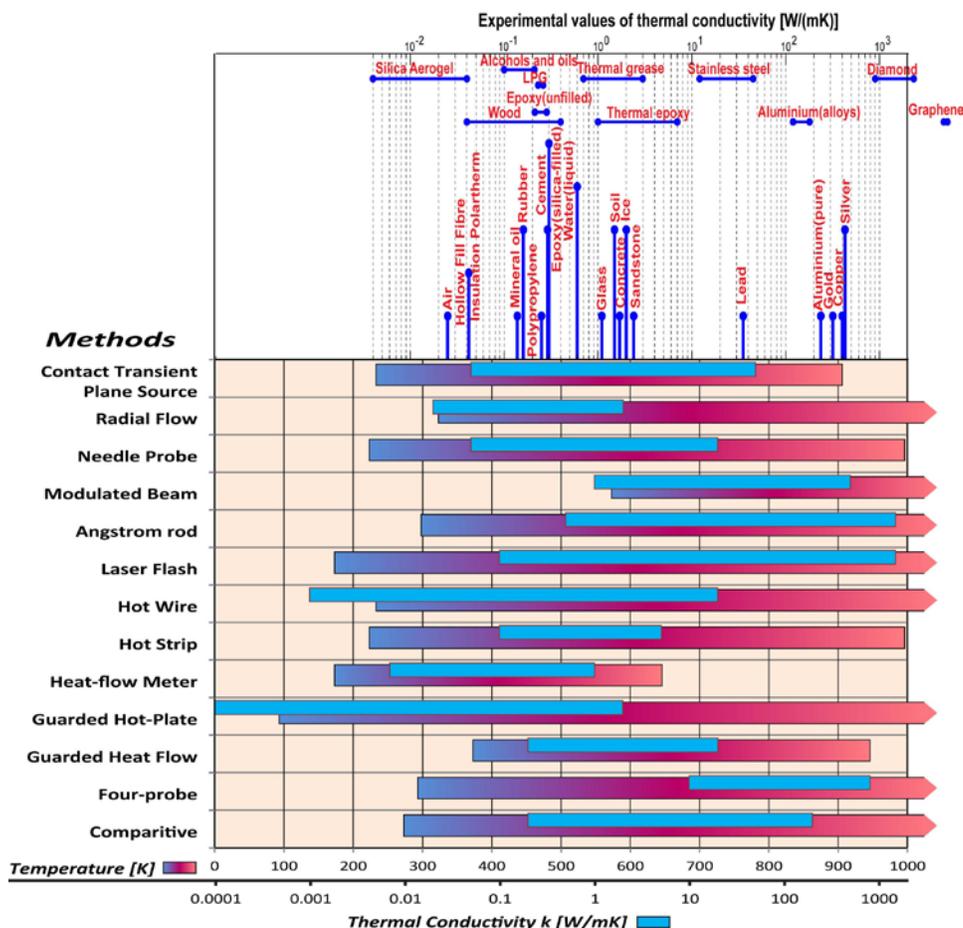


FIGURE 2. Example materials and common measurement methods for different ranges of thermal conductivity [2]

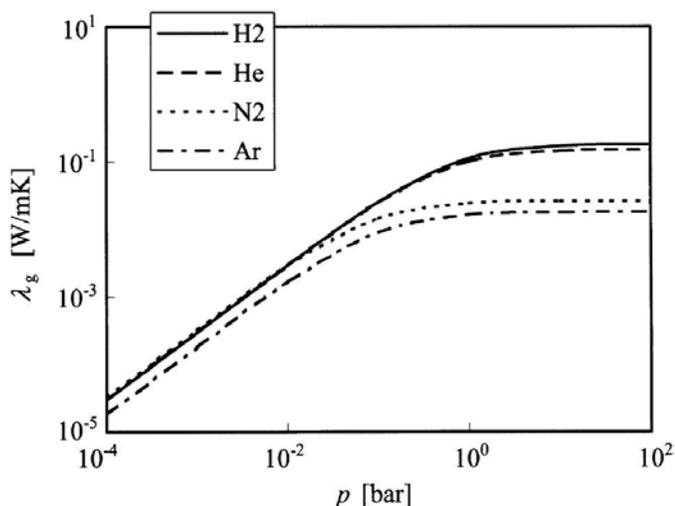


FIGURE 3. Effect of the pressure on the thermal conductivity of different gases [3]

Both methods were explored by Fedchnia et al. for both hydrides and physisorption materials [6]. In that study, three

materials, Ti-doped sodium aluminum hydride, an 8:3 mixture of lithium hydride and magnesium amide, and a metal organic framework were mixed with expanded natural graphite ‘worms’, and uni-axially pressed in a square die to compact the material into cube shaped samples. A hot disk thermal constants analyzer (Figure 6) was used to measure thermal conductivity. The analyzer supplies a constant power to an initially isothermal sample via a sensor located in the middle between two cubes shaped samples and follows, during a limited heating period, the resulting temperature increase using the same sensor also as a resistance thermometer.

The measurements revealed significant anisotropy in the thermal conductivity of these compacted powders. The study also found that there are several important considerations in performing an accurate analysis of thermal conductivity data. These are:

- Analytical solutions for the hot disc in infinite media becomes prohibitive for material exhibiting anisotropic properties.
- It also does not allow inclusion of the heat transfer coefficient for the boundary between the sensor and the material.

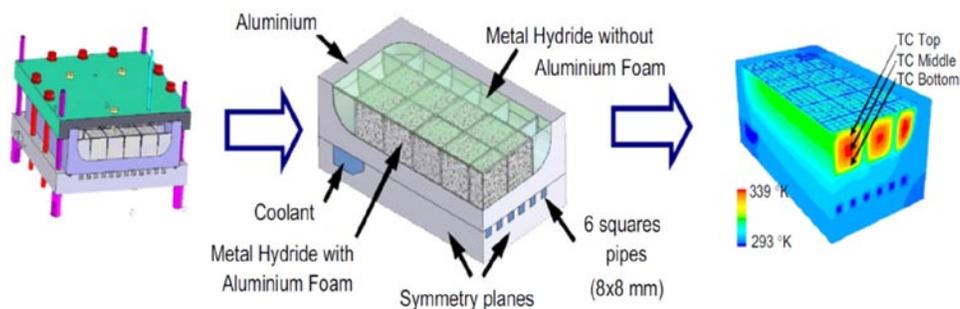


FIGURE 4. AB₅ hydride bed (left), its modeled geometry (center), and calculated temperature contours of temperatures (right) during absorption [5]

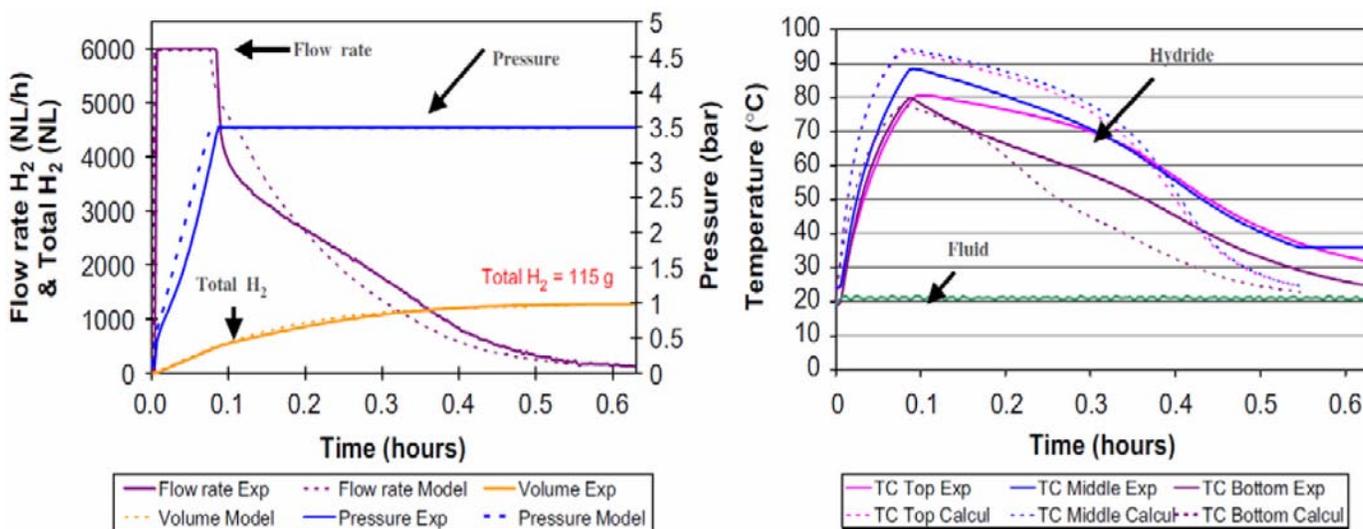


FIGURE 5. Experimental results vs. model results. The experimental results are plotted in continuous lines and the simulation results are plotted as dashed lines [5].

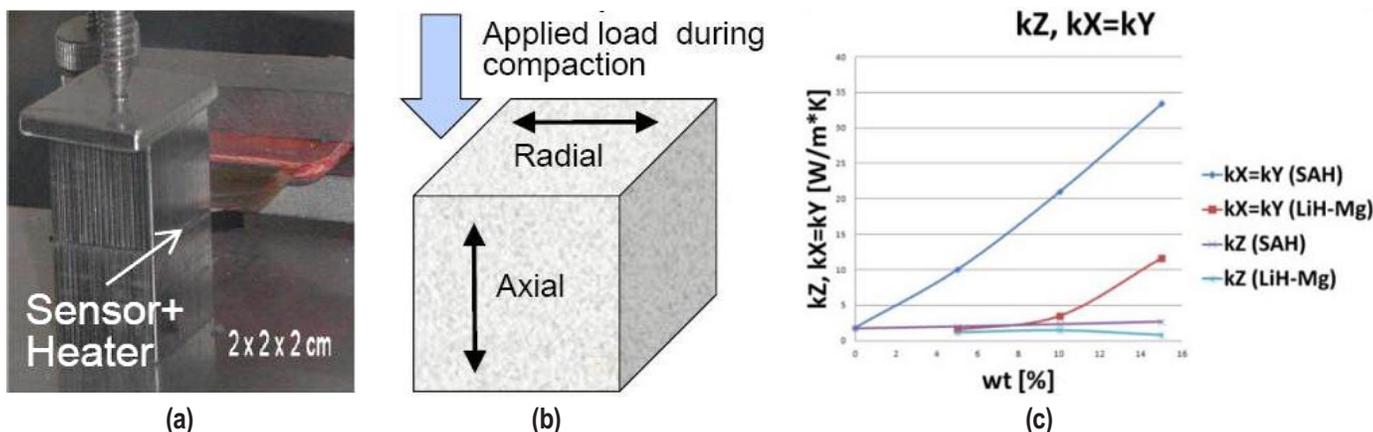


FIGURE 6. (a) Thermal measurement system, (b) Material compaction process, and (c) Thermal conductivity of sodium alanate as a function of thermal additives and direction [6]

- This becomes important for the materials modified by the applied stress. Not accounting for this leads to the wrong relation between the heat applied from the hot disc and the heat transfer properties of the material.
- Also, only thermal diffusivity can be estimated from the analytical model, heat capacity must be measured in a separate experiment.

Conclusions and Future Directions

In FY 2012 we were able to establish important collaborations and technical assistance from experts in the field. We were able to finalize the “Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials” sections 1-5 in a timely manner. We are currently working on completing the final version of the Engineering Thermal Properties measurements section and have initiated work on the Engineering Mechanical Properties measurement section.

FY 2012 Publications/Presentations

1. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S., Karkamkar, Dantzer, P., Ma, S., Zhou, H.C., Ott, K., Burrell, T., Semesberger, T., Pivak, Y., Dam, B., and Chandra, D. “Best Practices for Characterizing Hydrogen Storage Properties of Materials”, IEA HIA Experts Meeting, January 16 – 20, 2011, Fremantle, Australia.
2. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S., Karkamkar, A., Ma, S., Zhou, H.C., Dantzer, P., Ott, K., Burrell, T., Semesberger, T., Pivak, Y., Dam, B. and Chandra, D., “International standardized testing practices for hydrogen storage materials” IEA HIA Task 22 Expert Workshop for fundamental and applied hydrogen storage materials development, Copenhagen, Denmark, Sept. 6 2011.
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References

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2. Adapted from: Evitherm.org article, “Measurement Methods”, <http://www.evitherm.org/>, <http://www.evitherm.org/default.asp?ID=308>, and Wikipedia article “Thermal Conductivity”, http://en.wikipedia.org/wiki/Thermal_conductivity. http://en.wikipedia.org/wiki/Thermal_conductivity.
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