IV.E.7 Best Practices for Characterizing Engineering Properties of Hydrogen Storage Materials

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Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 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 program.

Technical Barriers

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

(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 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 H_2 from tank and impact on capacity and kinetic related targets)
- Cycle-Life Properties (Targets: cycle life and cycle life variation)

FY 2011 Accomplishments

- Modify 2010 Best Practices document with input from the National Renewable Energy Laboratory regarding clarifications of skeletal density and blank sample measurements.
- References collect for Cycle-Life section.
- Thermodynamics section input received and integrated from the Los Alamos National Laboratory.
- Received review of Thermodynamics section from Texas A&M University.
- Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents.
- Final Introduction section 100% complete.
- Final Kinetics section 100% complete.
- Final Capacity section 100% complete.
- Final Thermodynamic section in progress 95% complete.
- Final Cycle-Life Properties section in progress 95% complete.
- Draft Thermal Properties section started 15% complete.

- Posted updated Preface, Introduction, Kinetics and Capacity sections to DOE website for world-wide access. Please download the current document from: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html

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Introduction

The Hydrogen Storage 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 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 principal investigator 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.

The current document has been reviewed by many experts from around the world. We greatly appreciate the collaborative efforts of all of the reviewers: Professor Gavin Walker, University of Nottingham, United Kingdom; Dr. Thomas Gennett of the National Renewable Energy Laboratory in Golden, CO; Dr. Gary Sandrock and Dr. George Thomas, consultants to the U.S. Department of Energy; Dr. Michael Miller of Southwest Research Institute in San Antonio, TX; Dr. Anne Dailly and Dr. Frederick Pinkerton of General Motors R&D Center; Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller, Norway; Dr. Eric Poirier of NRC Canadian Neutron Beam Centre Chalk River Laboratories, Canada; Professor Channing Ahn of the California Institute of Technology in Pasadena, CA; Dr. Kevin Ott, Dr. Anthony Burrell, and Dr. Troy Semelsberger of Los Alamos National Laboratory; Professor Richard Chahine, Université du Québec à Trois-Rivières, Canada; Professor Klaus Yvon, University of Geneva, Switzerland; Professor Sam Mao of the University of California Berkeley in Berkeley CA; and Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi of the National Institute of Advanced Industrial Science and Technology in Osaka, Japan. In addition, the work has been coordinated and has received important scientific input through our contract monitor Dr. Phil Parilla at the National Renewable Energy Laboratory.

Results

This year the Best Practices document had updates to the capacity measurements based on the need to elucidate measurement issues associated with low density, high surface area materials. In particular, the problems of small sample size and potential calibration errors due to helium adsorption. The need for blank sample measurements to validate accuracy was also addressed. The updated version including a preface, introduction, kinetics and capacity measurement sections is now posted on the DOE website.

This year's work focused in large part on finalizing the Thermodynamics and Cycle-Life measurements sections of the "Best Practices" document. For this work collaborations were established with the following contributing authors: Pierre Dantzer, Université Paris-Sud; Shengqian Ma and Hong-Cai Zhou, Texas A&M University; Kevin Ott, Tony Burrell and Troy Semeslberger, Los Alamos National Laboratory; Yevheniy Pivak and Bernard Dam, VU University Amsterdam and Delft University of Technology; and Dhanesh Chandra of the University of Nevada Reno. A rigorous review of the Thermodynamics section was completed by Professor Gavin Walker of the University of Nottingham. Through these collaborations the document has added perspectives of critical measurement issues from the three main materials research areas: on-board rechargeable hydrides, off-board regenerable hydrides, and hydrogen physisorption storage materials.

The objective of the thermodynamic section of the Best Practices document is to evaluate methodologies for determining equilibrium thermodynamics. In particular, there is a need to shed light on how to separate true equilibrium conditions from kinetic effects. Examples are included below of recent additions incorporated into the thermodynamic measurements section. Figure 1 shows a unique setup for high-throughput measurements of the enthalpy of formation of thin film combinatorial samples using Hydrogenography [1]. This method uses the classic conversion of pressure-composition-temperature isotherms of a reversible hydride to a van't Hoff plot for the determination of the enthalpy and entropy of hydride formation.

Hydrogenography consists of measuring the log of the optical transmission by means of a charge-coupled device

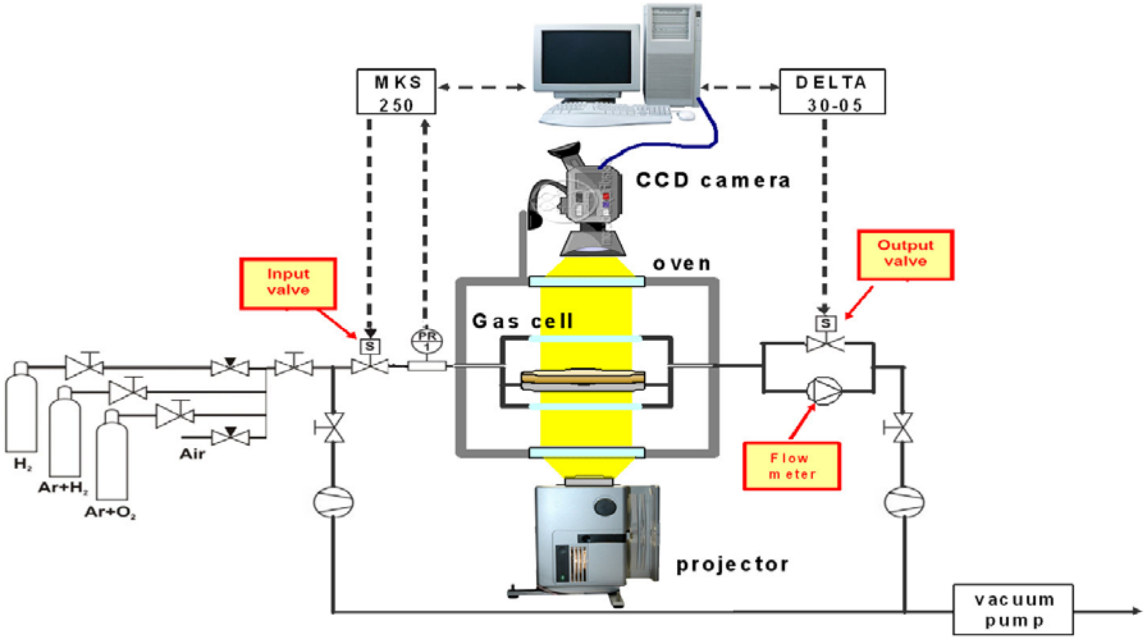

FIGURE 1. Schematic Representation of a Hydrogenography Setup [1]

camera through a thin film sample while increasing or decreasing the hydrogen pressure surrounding the sample. The optical transmission is proportional to the local hydrogen concentration of the material in the two-phase region. A rapid change in optical transmission indicates a hydride formation plateau. Thus, plateau pressures can be measured simultaneously at every point on two-dimensional combinatorial films having composition gradients. Repeating the measurement at several temperatures gives a van't Hoff plot for every point on the film and consequently every material composition. As an example of this, Figure 2 shows the phase diagram (left) and corresponding enthalpy map (right) of the Mg-Ni-Ti ternary system [2].

Cycle-life performance measurements are critical for evaluating the practical use of hydrogen storage materials in applications such as hydrogen-powered vehicles where hundreds to thousands of cycles will be required. An example of the impact on the hydrogen storage performance by making small changes in composition of the intermetallic compound $LaNi_5$ is show below in Figure 3.

The Cycle-Life measurement section covers the advantages and disadvantages of different measurement methods. For example, measurements of the cycle-life performance of hydrogen storage materials can be performed using pressure-temperature cycling or, in some cases, far more quickly by performing a thermal aging process on test

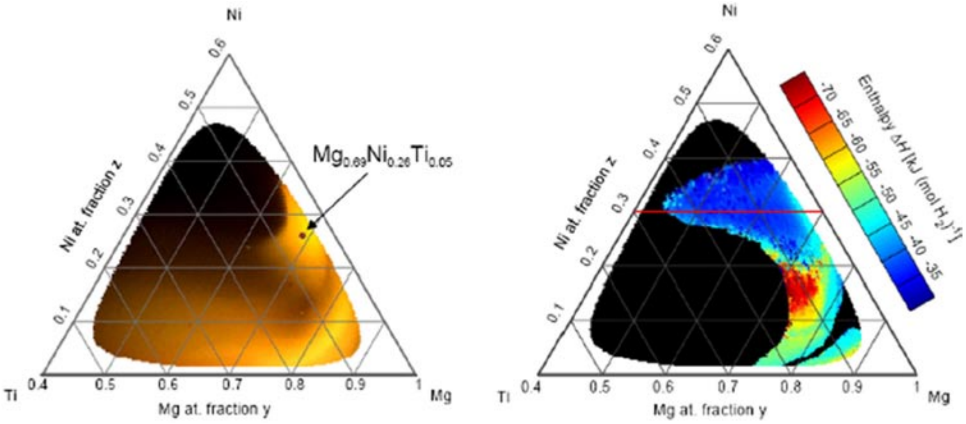

FIGURE 2. Ternary composition diagram (left) showing the final optical transmission state and the enthalpy map (right) of the Mg-Ni-Ti system, estimated using the optically determined hydrogenation plateaus. Black region on the right-hand picture represents chemical compositions that do not have a well defined plateau on the pressure-temperature isotherms [2].

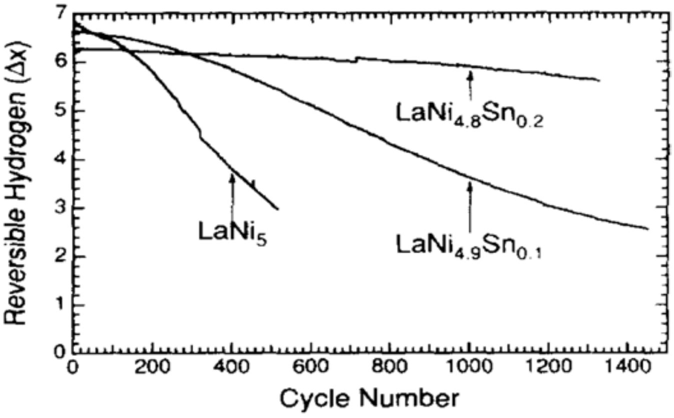

FIGURE 3. Hydrogen concentration changes Δx for $LaNi_{5-y}Sn_yH_x$ obtained from the maximum and minimum pressures for each cycle [3].

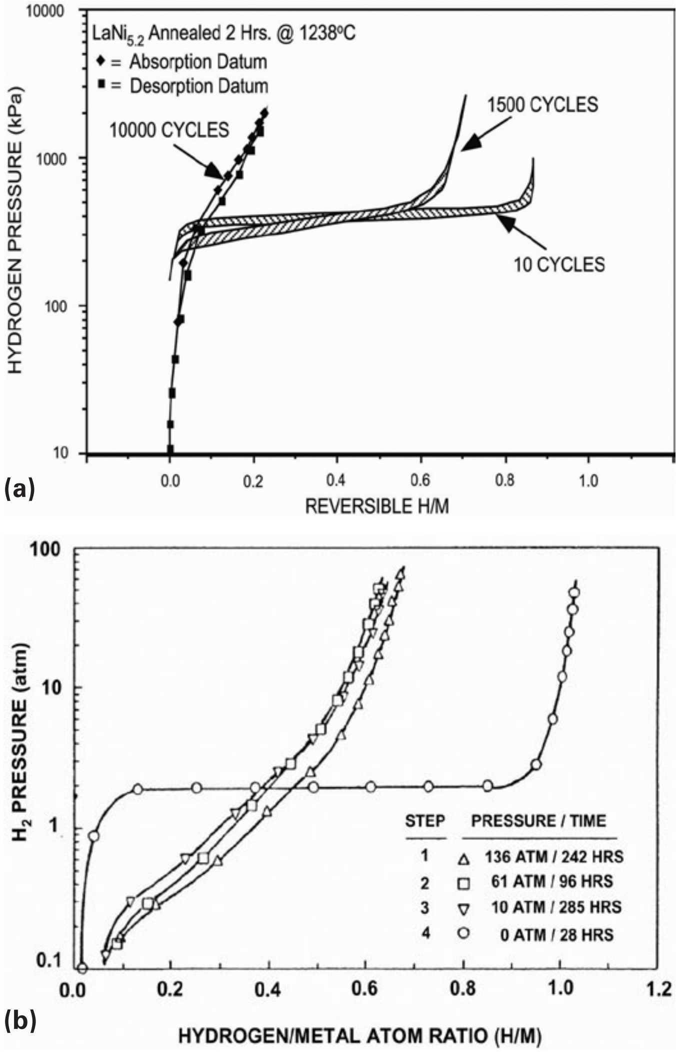

FIGURE 4. a) Isotherm of $LaNi_{5.2}$ taken at 25°C after intrinsic pressure-temperature cycling for: 10 (activation), 1,500, 10,000 cycles, showing severe degradation of this hydride [4]. b) Isotherms of $LaNi_5$ taken at 25°C after subjecting to thermal aging at high and low hydrogen pressures. Note that the isotherm (4) after vacuum aging the sample at 180°C is nearly the same as before aging indicating full reproportionation of the $LaNi_5$ hydride [5].

samples. In both cases, the measurements can be used to evaluate intrinsic performance degradation by using closed system designs which continuously cycle the same hydrogen gas. A comparison of results for $LaNi_5$ alloys using these two different methods and giving similar results is shown in Figure 4.

Conclusions and Future Directions

In FY 2011 we were able to establish important collaborations and technical assistance from experts in the field. We were able to update the Capacity section in a timely manner. We are currently working on completing the final versions of the Thermodynamic and Cycle-Life measurement sections.

FY 2011 Publications/Presentations

1. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S. Karkamkar, Dantzer, P., Ma, S., Zhou, H.C., Ott, K., Burrell, T., Semeslberger, T., Pivak, Y., Dam, B., and Chandra, D. "Best Practices for Characterizing Hydrogen Storage Properties of Materials", IEA HIA Experts Meeting, April 11–15, 2010 in Death Valley, CA USA.

2. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S. Karkamkar, Dantzer, P., Ma, S., Zhou, H.C., Ott, K., Burrell, T., Semeslberger, 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.

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4. Chandra, D., "Intermetallics for hydrogen storage", in the book "Solid-state hydrogen storage, Materials and chemistry", edited by Gavin Walker, (2008) Woodhead Publishing Limited, Cambridge England, CRC Press, 327.

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