IV.E.6 Best Practices for Characterizing Hydrogen Storage Properties of Materials

Karl J. Gross (Primary Contact),
Russell Carrington[1], Steven Barcelo[1],
Abhi Karkamkar[2], Justin Purewal[3],
Pierre Dantzer[4], Shengqian Ma and
Hong-Cai Zhou[5], Kevin Ott, Tony Burrell
and Troy Semeslberger[6], Yevheniy Pivak and
Bernard Dam[7], Dhanesh Chandra[8]
H2 Technology Consulting LLC
8440 Central Ave. Suite 2A
Newark, CA 94560
Phone: (510) 402-4848
E-mail: kgross@h2techconsulting.com
[1] University of California, Berkeley
[2] Pacific Northwest National Laboratory
[3] California Institute of Technology
[4] Université Paris-Sud
[5] Texas A&M University
[6] Los Alamos National Laboratory
[7] VU University Amsterdam and the Delft University of Technology
[8] University of Nevada, Reno

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152
E-mail: Carole.Read@ee.doe.gov

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

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 (International Energy Agency/International Partnership for the Hydrogen Economy, etc.).
- 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).

Accomplishments

- Established new collaborations with: Université Paris-Sud, Texas A&M University, Los Alamos National Laboratory, VU University Amsterdam/Delft University of Technology and University of Nevada, Reno.
- Compiled example measurements from the literature, to illustrate key issues associated with the four tasks outlined above.
- Performed example measurements to illustrate key issues associated kinetics and other measurements.
- 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.
- Draft Thermodynamic section in progress 85% complete.

- Draft Cycle-Life Properties section in progress 50% complete.
- Posted final reviewed Preface, Introduction, Kinetics and Capacity sections to DOE Web site for world-wide access. Please download the current document from: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage.pdf

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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 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.

In Fiscal Year (FY) 2010 sections of the document were reviewed by many experts from around the world. We greatly appreciate the collaborative efforts of all of the reviewers: Dr. Thomas Gennett of the National Renewable Energy Laboratory, Dr. Gary Sandrock and Dr. George Thomas, consultants to the U.S. Department of Energy, Dr. Michael Miller of Southwest Research Institute®, 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, Professor Channing Ahn of the California Institute of Technology, Dr. Kevin Ott, Dr. Anthony Burrell, and Dr. Troy Semelsberger of Los Alamos National Laboratory, Professor Richard Chahine, Université du Québec à Trois-Rivières, Professor Klaus Yvon, University of Geneva, Professor Sam Mao of the University of California, Berkeley, 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

The second task in this project focused on creating a best practices document for capacity measurements. This has been completed reviewed and public commentary has be received and addressed. The final version including a preface, introduction, kinetics and capacity measurement sections is now posted on the DOE Web site.

In addition, this year's work covered 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 Dahnesh Chandra of the University of Nevada, Reno. 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.

Examples are included below of important considerations when making thermodynamic measurements. Figures 1 shows the classic conversion of pressure-concentration-temperature (PCT) isotherms of a reversible hydride to a van't Hoff plot for the determination of the enthalpy and entropy of hydride formation.

This simplified example does not take into consideration, irreversibilities that lead to hysteresis between absorption and desorption measurements. It also depicts the thermodynamic behavior a highly ordered crystalline material as opposed to real materials which range from some structural defects, may also include multiple partial substitutions, to fully amorphous materials. As an example of this, Figure 2 shows

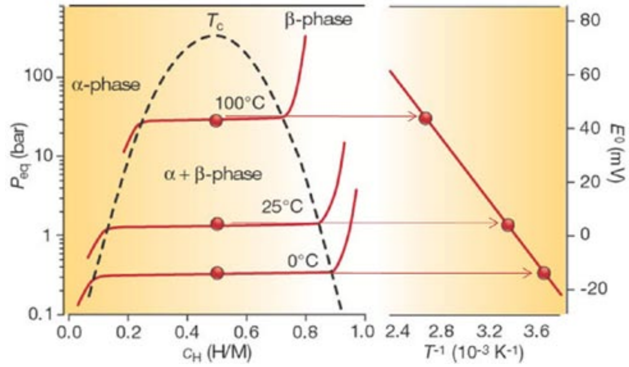

FIGURE 1. Example of the Construction of a van't Hoff Plot from a Series of PCT Measurements

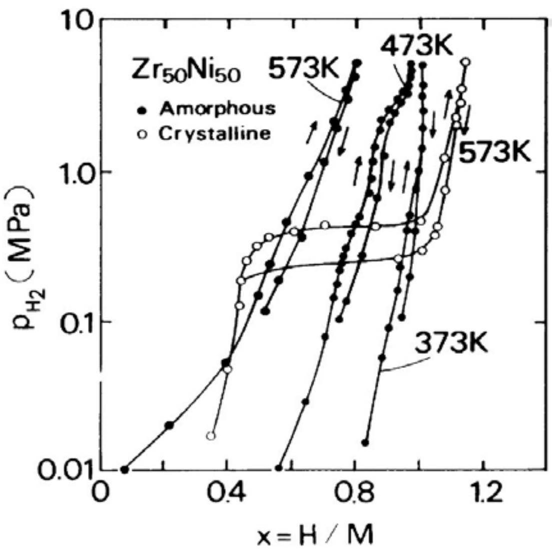

FIGURE 2. PCT plots for amorphous and crystalline $Zr_{50}Ni_{50}$. The amorphous measurements do not show a pressure plateau [1].

significant differences the PCT plateau behavior of crystalline to amorphous ZrNi-hydrides.

The heat of reaction in storing hydrogen in a hydride consists of the heats of hydrogen solution as well as hydride formation. In this respect the total heat produced (as measured by calorimetry) will not necessarily be the same as the enthalpy of hydride formation (as measured by the van't Hoff method). Figure 3 depicts the complete hydrogen absorption of a material where hydrogen is absorbed first in solution, then forms a hydride and finally further dissolution of hydrogen into the hydride. In this sense, the Van't Hoff measurements based on plateau pressures only are useful in comparing the stability differences between hydrogenated compounds, however they may not

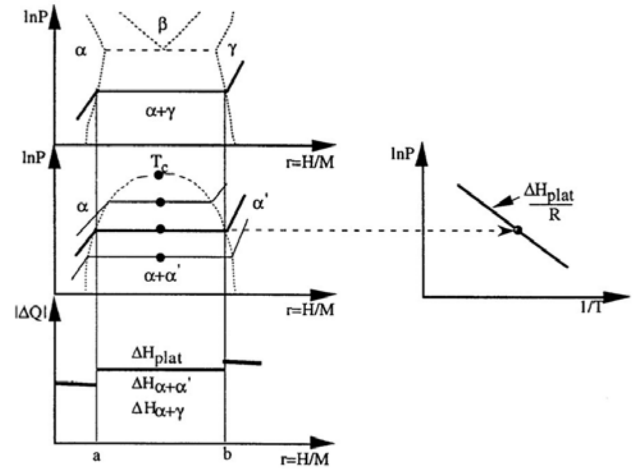

FIGURE 3. Ideal case, reversible conditions. Top-Left) isotherm in which hydrogen induces a structural change, Middle-Left) isotherms in which the structure is maintained. Right: Van't Hoff plot. The line must stop at Tc. Bottom-Left) heat evolved during the abs/des processes [2].

fully represent the heat produced (or required) in real hydrogen storage applications.

With physisorption storage materials, the determination of isosteric heat of adsorption for hydrogen is an important aspect of characterizing the potential of porous materials for on-board hydrogen storage applications. By drawing the ln pressure vs. 1/temperature plot of H_2 at various hydrogen concentrations, the isosteric heat of adsorption can be determined (Figure 4).

Conclusions and Future Directions

In FY 2010 we were able to establish important collaborations and technical assistance from experts in the field. We were able to complete the final version of the Capacity section in a timely manner. We are currently working on the Thermodynamic and Cycle-Life measurement sections. We expect to complete the draft version these sections in this fiscal year.

FY 2010 Publications/Presentations

1. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S., Karkamkar, A. "Best Practices for Characterizing Hydrogen Storage Properties of Materials", IEA HIA Experts Meeting, Shilla Jeju Hotel, Jeju Island, Korea, 19-23 April 2009.

2. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S., Karkamkar, A. "Best Practices for Characterizing Hydrogen Storage Properties of Materials", IEA HIA Experts Meeting, Paris, France, 12–15 October 2009.

3. Gross, K.J., Carrington, R., Purewal, J., Barcelo, S., Karkamkar, A., 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

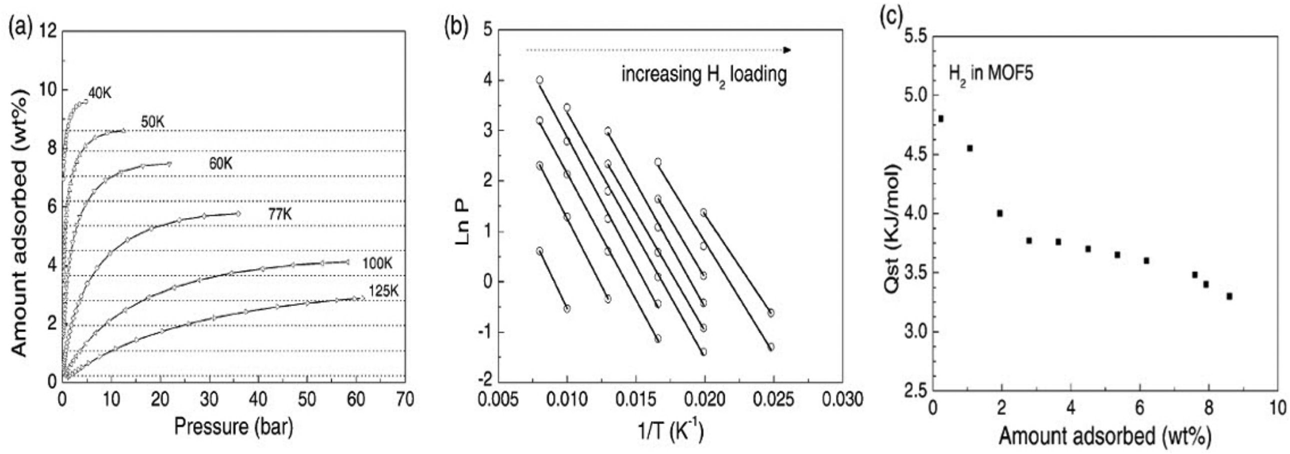

FIGURE 4. (a) Excess adsorption isotherm data of H_2 in the MOF-5 metal-organic framework storage material, used in the heat of adsorption calculation. Dotted lines indicate pressure-temperature data at fixed hydrogen concentrations. (b) The ln pressure vs. 1/temperature plot of H_2 in MOF-5 at various wt%. According to the Clausius-Claperyron equation, the isosteric heat of adsorption Qst = -slope × R. (c) Qst plot for H_2 adsorption in MOF-5, as derived from (b) [3].

Storage Properties of Materials", IEA HIA Experts Meeting,11–15 April 2010 in Death Valley, CA USA.

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3. Zhou, W., Wu, H., Hartman, M. R., Yildirim, Taner "Hydrogen and Methane Adsorption in Metal-Organic Frameworks: A High-Pressure Volumetric Study." J. Phys. Chem. C 111 (2007): 16131-16137.