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

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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 (IEA)/ 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Technical Targets: On-Board Hydrogen Storage Systems
- Barriers addressed
  - (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 Pacific Northwest National Laboratory, the University of California, Berkeley, and California Institute of Technology.
- Compiled example measurements from the literature to illustrate key issues associated with the four tasks outlined above.
- Performed example measurements on classic hydride materials 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.
- Capacity section in progress 60% complete.
- Posted final reviewed Preface, Introduction, and Kinetic sections to DOE Web site for world-wide access.
- The current Best Practices document is available on the Web [1].

- Presentation: project H-27 "International standardized testing practices for hydrogen storage materials" IEA Hydrogen Implementing Agreement (HIA) Task 22 Expert Workshop for fundamental and applied hydrogen storage materials development. October, 6–10, 2008, Villa Mondragone, Rome, Italy.

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Introduction

The Hydrogen Storage 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 U.S. DOE Hydrogen Storage 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 measurements, incorporating examples from the literature, performing experimental measurements to demonstrate important issues, and finally, condensing key information into a concise reference guide. Participation from other experts in the field is being sought out for input, relevant examples, and critical review at all levels.

Results

The first task in this project focused on creating a best practices document for kinetics measurements as well as a general introduction and a preface section of the overall "Best Practices" document. The preface section includes a foreword and terminology used throughout the Best Practices document. The introduction section includes an overview of hydrogen storage materials and the common techniques used to characterize the storage properties of such materials. The kinetics section covers such topics as the overall purpose of kinetics measurements, some basic theory, experimental consideration depending on the purpose of the measurements, methods of measurement, and many details on both material properties and experimental factors that may strongly influence the final results and conclusions.

In Fiscal Year 2009 these sections of the document were reviewed by many experts and after integration of all comments and edits the final version of these sections was posted on the U.S. DOE Web site. We greatly appreciate the collaborative efforts of Professor Sam Mao and Russell Carrington of the University of California, Berkeley and the work of all of the reviewers: 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, Dr. Eric Poirier, and Dr. Frederick Pinkerton of General Motors R&D Center; Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller, Norway; Professor Channing Ahn of the California Institute of Technology in Pasadena, 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.

The next task focused on the capacity section of the "Best Practices" document. For this work collaborations were established with the following contributing authors: Steven Barcelo from the University of California, Berkeley, Justin Purewal from the California Institute of Technology and Abhi Karkamkar from Pacific Northwest National Laboratory. Through this collaboration the document has added perspectives of critical measurement issues from the three main materials research areas: on-board rechargeable chemical hydrides, off-board regenerable chemical hydrides, and hydrogen physisorption materials. The first draft of this section has been completed and sent to several reviewers.

Examples are included below of important considerations when making capacity measurements on different types of materials. Figure 1 shows hydrogen desorption capacity increase for the on-board rechargeable chemical hydride, Ti-doped $NaAlH_4$, during initial activation cycles [2]. Several cycles may be required to reach full capacity and materials should not necessarily be overlooked because of poor capacity in only the first absorption/desorption cycle.

Figure 2 shows significant differences in capacity at different temperatures for the off-board regenerable chemical hydride, ammonia borane. Changes in the induction period as a function of temperature are observed and are due to changes in the chemical process pathways at different temperatures [3].

Figure 3 demonstrates the difference between measured excess capacity and the total material hydrogen capacity for metal-organic framework (MOF) physisorption materials [4].

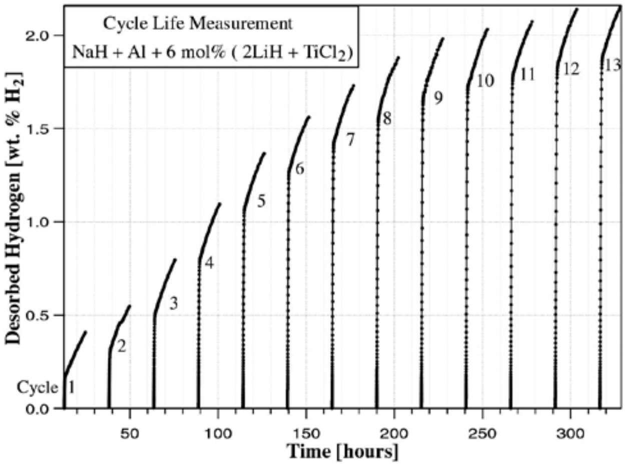

FIGURE 1. Example of activation effects on capacity for hydrogen release from $NaAlH_4$ doped with pre-reacted Ti additive [2].

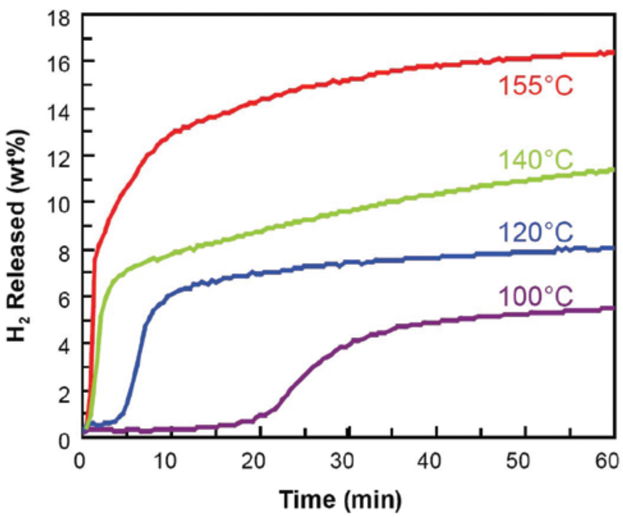

FIGURE 2. Dehydrogenation capacity as a function of time and temperature for ammonia borane [3].

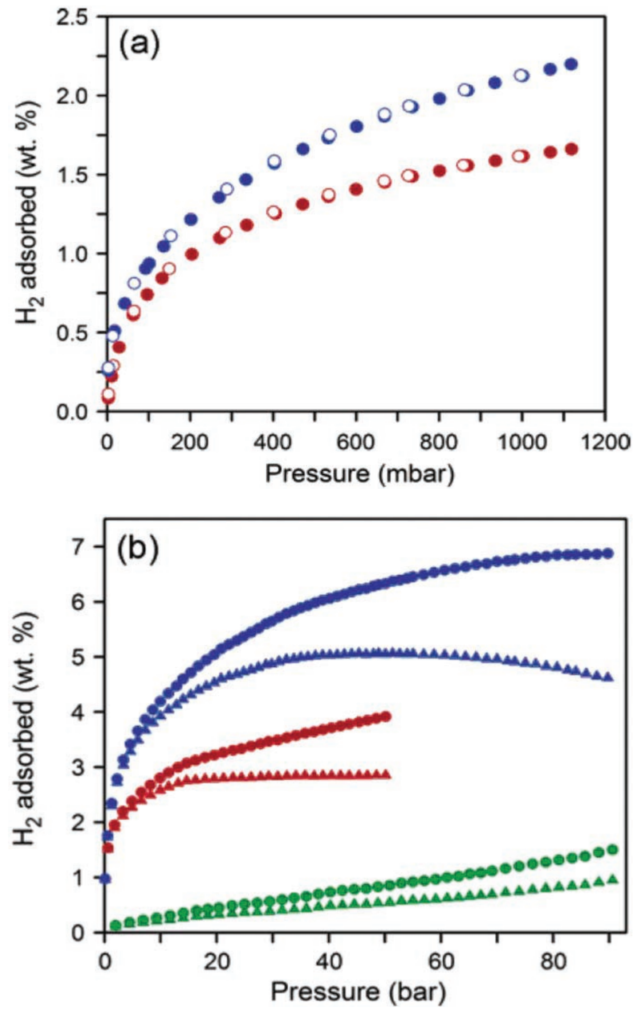

FIGURE 3. H_2 adsorption isotherms (a) below 1.2 bar and (b) up to 90 bar MOFs 1′ (red) and 1m′ (blue) at 77 K, and 1m′ at 298 K (green). Triangles = Material Excess Capacity. Circles = Total Material Capacity [4].

Conclusions and Future Directions

In FY 2009 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 preface, introduction and kinetics sections in a timely manner. We are currently working on the capacity section. The first draft of this section has been completed and sent to reviewers. We expect to complete the final version of the capacity section this fiscal year. The following tasks will be the focus of our work in the future:

- Thermodynamics
  - The objective of this task is to establish methodologies for determining equilibrium thermodynamics of hydrogen storage materials.
  - We will define measurement protocols to separate true equilibrium conditions from kinetic effects and evaluate new measurement techniques for the rapid determination of thermodynamic stabilities.
- Cycle-life Properties
  - This task will focus on better definitions of how such tests should be performed.
  - We will detail what parameters may impact results, and what properties are the most critical in performance evaluation.

FY 2009 Publications/Presentations

1. Presentation: Gross, K.J., Carrington, R., "Characterization of Advanced Hydrogen Storage Materials: Best Practices in Measurements", International Symposium on Metal-Hydrogen Systems, June 24-28, 2008, Reykjavik, Iceland.

2. Presentation: project H-27 "International standardized testing practices for hydrogen storage materials" IEA HIA Task 22 Expert Workshop for fundamental and applied hydrogen storage materials development. 2–5 March 2008, Sacacomie, Québec, Canada.

References

1. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf

2. K.J. Gross, E.H. Majzoub, S.W. Spangler, J. Alloys and Compounds, 356-357 (2003) 423.

3. C. Aardahl, T. Autrey, J. Linehan, D. Camaioni, S. Rassat, D. Rector, W. Shaw, J. Li, D. Heldebrant, A. Karkamkar, FY2007 PNNL Progress within the DOE Center of Excellence for Chemical Hydrogen Storage.

4. M. Dinca et al. "Hydrogen Storage in a Microporous Metal-Organic Framework with Exposed Mn2+ Coordination Sites", J. Am. Chem. Soc. 2006 128, 16876-16883.