

IV.C.2 Hydrogen Sorbent Measurement Qualification and Characterization

Philip A. Parilla (Primary Contact),
Katherine Hurst, Michele Olsen, Thomas Gennett
National Renewable Energy Laboratory (NREL)
15013 Denver West Pkwy.
MS 3219
Golden, CO 80228
Phone: (303) 384-6506
Email: Philip.Parilla@nrel.gov

DOE Manager

Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@ee.doe.gov

Collaborators

- Karl Gross, H2 Technology Consulting LLC, Fremont, CA
- Jeff Long group, University of California, Berkeley, Berkeley, CA
- Joe Zhou group, Texas A&M University, College Station, TX
- Seth Cohen group, University of California, San Diego, San Diego, CA
- Hydrogen Storage Technical Team
- Troy Semelsberger, Los Alamos National Laboratory, Los Alamos, NM
- Craig Brown, National Institute of Standards and Technology, Gaithersburg, MD

Project Start Date: October 1, 2012

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

ultimate goal of assisting materials-research groups to characterize and validate their thermal conductivity measurements

Fiscal Year (FY) 2015 Objectives

- Disseminate volumetric capacity protocols and recommendations for their implementation to the hydrogen storage community so that material properties can be reported in a uniform and unambiguous manner
 - Give input to and receive feedback from the Hydrogen Storage Technical Team on previously developed protocols and recommendations for determining and reporting on volumetric capacity for hydrogen storage materials
 - Submit a report that will be disseminated to the scientific community (pending at the time of this report)
- Develop an in situ thermal conductivity measurement capability for hydrogen storage materials for measurements from 77 K to 400 K and at ambient gas pressures up to 150 bar
 - Establish methodology for characterizing materials with different form factors
 - Design and integrate components for the measurement system
 - Validate measurement technique over entire temperature and pressure range
- Assist materials research groups to characterize and qualify their samples for hydrogen storage properties
 - Measure external samples at NREL to compare results with source group's and/or third party's results
 - Discover sources of measurement discrepancies and advise on corrective actions, if needed, for source group
- Analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric and TPD systems
 - Analyze realistic models for random and systematic errors
 - Identify the major error sources that will dominate the measurement
 - Recommend improved instrumentation and procedures to minimize such errors

Overall Objectives

- Provide validation measurements for the hydrogen capacity of storage materials
- Develop and disseminate measurement best practices and recommended protocols and data analysis procedures for hydrogen capacity measurements
- Assist research groups within the hydrogen storage community to perform robust and accurate measurements of hydrogen storage capacity
- Analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric and temperature programmed desorption (TPD) systems
- Develop an in situ thermal conductivity measurement capability for hydrogen storage materials with the

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life-Cycle Assessments
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (P) Reproducibility of Performance

Technical Targets

This project supports the following overall DOE objective: “Capacity measurements for hydrogen-storage materials must be based on valid and accurate results to ensure proper identification of promising materials for DOE support.” Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage material systems that meet the 2020 DOE hydrogen storage targets:

- Cost: \$10/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

The specific technical objectives include:

- Disseminate measurements qualification and validation improvements to the hydrogen community
- Work with hydrogen storage material-synthesis researchers to measure, at least, two external samples.

FY 2015 Accomplishments

- Developed recommended volumetric capacity definitions and protocols that were thoroughly described in a report
 - Presented findings at the International Energy Agency-Hydrogen Implementing Agreement Task in Chamonix, France, January 2015
 - Presented findings before the Hydrogen Storage Technical Team, which subsequently provided feedback that was incorporated into the document
 - Will publish manuscript in a special edition for hydrogen storage in Applied Physics A

- Completed initial work for an in situ thermal conductivity measurement system for hydrogen storage materials
 - Developed thermal modeling and established the viability of the single-sided transient plane source technique for measuring the thermal conductivity
 - Designed two “plug-and-play” modules that will enable thermal conductivity measurements of samples with volumes ranging from 0.5–60 cm³
 - Designed and assembled an instrument that includes temperature and pressure controls, capable of measuring the thermal conductivity of hydrogen sorption materials between 77 K and 400 K and at pressures up to 150 bar.
- Measured four external samples from outside laboratories, surpassing the milestone of measuring two external samples



INTRODUCTION

The ultimate goal of the Hydrogen Storage sub-program is the development of hydrogen storage systems that meet or exceed the DOE’s goals for onboard storage in hydrogen-powered vehicles. In order to develop new materials to meet these goals, it is extremely critical to accurately, uniformly, and precisely measure the materials’ properties relevant to the specific goals; otherwise the metrics are meaningless and achieving of goals, uncertain. In particular, capacity measurements for hydrogen-storage materials must be based on valid and accurate results to ensure proper identification of promising materials for DOE support. This project focuses on maintaining a world-class measurement facility for determining hydrogen storage capacities of novel research materials, understanding the experimental issues, procedures, and analysis to ensure accurate measurements, and assisting the hydrogen storage community in performing and understanding these measurements. NREL’s main focus is on the manometric measurement technique; this technique is also known as the volumetric and Sieverts technique.

Another important aspect for hydrogen storage systems is the thermal conductivity of the storage material used in the system because it impacts the design of heat exchangers necessary for temperature control during charging and discharging of the hydrogen. Low thermal conductivity (TC) materials require additives such as graphite and/or macroscopic heat transfer enhancing structures such as fins in the storage vessel. Furthermore, the TC of these materials depends on both temperature and the hydrogen gas pressure. To design proper thermal management for a given material, therefore, requires knowledge of the TC under the expected

operating conditions. For hydrogen sorption materials, the required temperatures may be as low as 77 K and pressures easily reaching 150 bar. An apparatus that can measure materials over the desired temperature and pressure range is not commercially available and requires customization.

APPROACH

NREL continues with a multiyear intensive effort to improve measurement quality and accuracy, understand the sources of and correct for measurement error, work with external groups to provide measurements and verify results, and collaborate with the hydrogen community to improve measurements. NREL had previously managed the “Best Practices” Project to disseminate recommended practices and procedures [1]. The approach for measurement quality and accuracy can be divided into three components (1) work with external groups to measure samples and to examine their measurement techniques and procedures; (2) analyze for, identify, and recommend corrective actions for major sources of measurement error in manometric systems; and (3) develop standardized procedures and protocols so that data and results are reported in a uniform manner to allow direct comparison of material performance. In this fiscal year, NREL has further developed definitions and implementations for determining volumetric capacity of hydrogen storage materials and has focused on producing a document describing these definitions and protocols with extensive input from the hydrogen storage community.

For a TC apparatus, measurements must be performed over a wide range of temperatures and pressures and capable of measuring small samples with different form factors such as pucks and powders. To facilitate facile throughput of sample measurements, it is desirable that these measurements be done quickly. We surveyed both steady-state and transient techniques, and identified the transient plane source technique as meeting these requirements. In its traditional application, a combined heater/sensor is sandwiched between two identical samples of the material under test. At time $t = 0$, constant power is applied to the heater, and the temperature change of the sensor as a function of time is fit to a model to obtain the TC and diffusivity of the material. The requirement of two samples with a minimum volume of $\sim 0.5 \text{ cm}^3$ can be prohibitive to materials research groups developing novel materials. To limit the quantities needed, we endeavored to develop a single-sided technique in which the sensor is placed between the sample under test and a sample of a material with known (and reasonably insulating) thermal properties. While this technique is incorporated into some commercial instruments, the technique is not published in the literature. To understand the impact of the reference material, we developed a thermal model of the technique. Because the model requires experimental validation, the TC apparatus will allow for both single-sided and traditional, double-sided transient plane source (TPS) measurements.

With respect to working with external groups, NREL actively seeks out collaborations for comparison studies, helps with DOE projects to ensure robust measurements, and tests very promising results for verification. Additionally, NREL works with external groups to discover sources of measurement discrepancies and provides advice on corrective actions, if needed. This work entails sending standardized samples to external labs to test instrumentation and experimental procedures, examining data and data analysis protocols to discover possible avenues to improve measurement techniques, and making recommendations to labs for improvements.

RESULTS

1. Continued to develop recommended volumetric capacity (VC) definitions and protocols and incorporate them into a report with input from the hydrogen storage community. VC determinations ultimately involve a separate accounting of hydrogen in a storage vessel or system and a separate accounting of quantifying the volume of said vessel or system and dividing the former by the latter. Different accountings for hydrogen and volumes define different figures of merit (FOMs) and depending on the goals of the project with corresponding emphasis of different merits, the best FOM to use to quantify those merits will change with the emphasis. Seven FOMs have been described and are recommended in the report that has been invited to be published in a special issue on hydrogen storage in Applied Physics A.
2. We developed a thermal model of the TPS techniques using COMSOL Multiphysics. With this model, we were able to simulate the single-sided TPS technique using the thermal properties of various real and fictitious materials. The fictitious materials allowed the thermal conductivity or diffusivity to be held fixed to determine the impact of the other parameters on the temperature increase at the sensor. In this way, the basic dependencies on the parameters were identified. Figure 1a shows a cross-sectional view of the modeled temperature profile within two dissimilar materials. Figure 1b shows the modeled temperature increase at the sensor as a function of time for single-sided TPS measurements with various sample materials (see legend in Figure 1c) and the reference material is polymethyl methacrylate (PMMA). Figure 1c shows the scaled simulated temperature increase as a function of a proposed time scaling that approaches a universal curve for all the simulated materials. Using this proposed scaling, we expect to be able to measure both the TC and thermal diffusivity of unknown materials, and the model will be experimentally validated.

For the overall TC apparatus, we have customized commercial instruments to achieve the required pressure

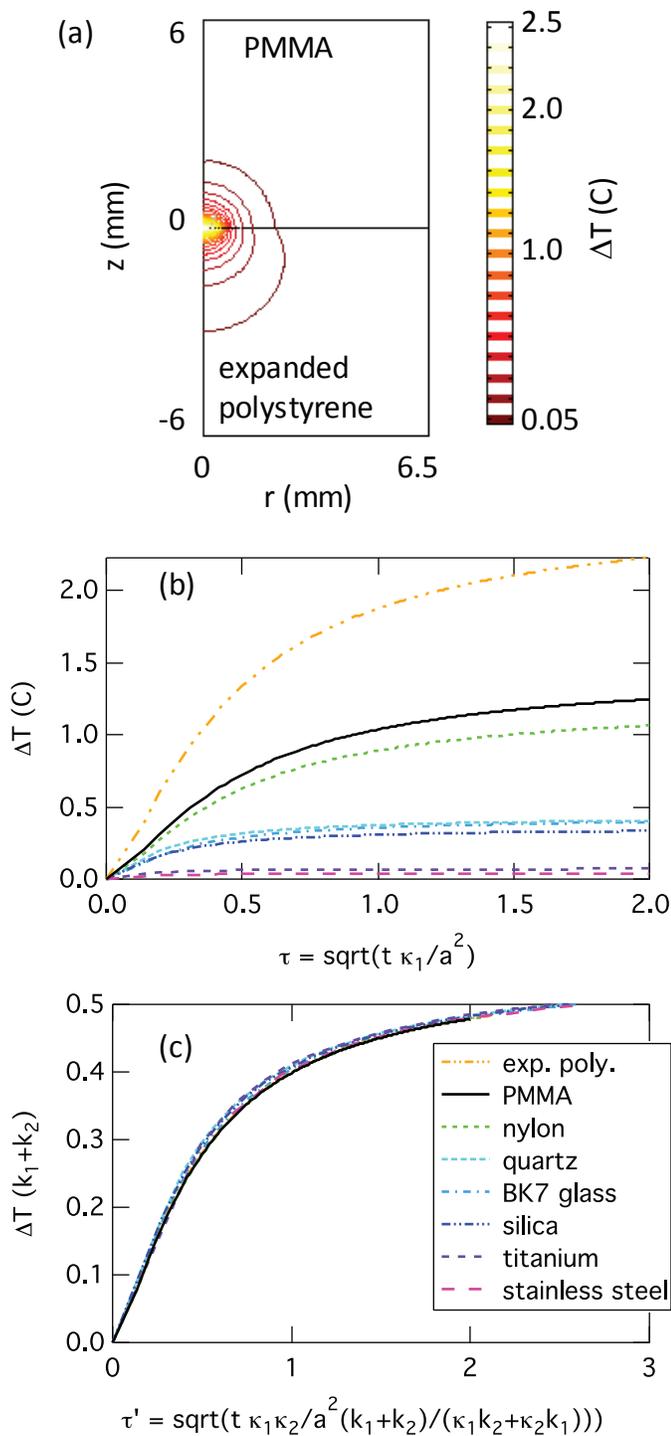


FIGURE 1. Thermal modeling of single-sided TPS measurements: (a) simulated temperature profile within two dissimilar materials, (b) temperature increase at the sensor as a function of time for a variety of materials, and (c) proposed scaling to extract thermal properties from single-sided TPS measurements

and temperature range. It consists of a cryostat from Advanced Research Systems that has a temperature range between 2 K and 400 K, and has been customized to include a high-pressure hydrogen inlet. There is also a customized pressure vessel from Parr Instruments with the necessary gas port and electrical feed-throughs for the TC measurement. To measure a sample, the sensor and sample are mounted inside the pressure vessel, and as shown in Figure 2a, the vessel is mounted on the cold head of the cryostat, the radiation shield (lower left) is mounted around the pressure vessel, and the entire system is enclosed within the vacuum shroud of the cryostat. We are designing several measurement “modules” that are plug-and-play sensor and sample holders for mounting samples with different form factors within the pressure vessel. Figure 2b shows the design of a module for measuring 13-mm diameter pucks with the single-sided TPS technique.

3. Measured four external samples from outside laboratories. This number surpasses the milestone of measuring two external samples. Each sample typically undergoes approximately nine measurements using different techniques in the course of a typical analysis. Techniques include multiple pressure-composition-temperature (PCT) isotherms, Brunauer-Emmett-Teller isotherm for surface-area analysis, TPD during degas, TPD after PCT, density and cycle-life PCT. Sample material types have included high-surface-area carbons with and without catalysts, BC_x (a boron substituted carbon material formed by the pyrolyzation of triethylborane) with and without catalysts, and metal organic frameworks (MOFs) with and without catalysts. Data from these external samples are considered proprietary.
4. Continued to develop realistic models for the data analysis for manometric systems, both for isothermal and non-isothermal conditions. The importance of using realistic models should not be underestimated. Volumetric mass-balance models in the scientific literature, although ideally correct, typically do not account for real-world measurement situations. Most volumetric systems contain many more moles in the gas phase than the moles sorbed onto the sample, thus requiring very accurate mass-balance accounting. We have concluded that the most dominant errors are still systematic errors! The main sources of systematic error are improper “null” calibration, inadequate data analysis models (mass-balance models), ignorance of the large error associated with non-uniform temperature fluctuations, and importance of having adequate sample mass and inexperience leading to undeserved trust in results (black-box syndrome).

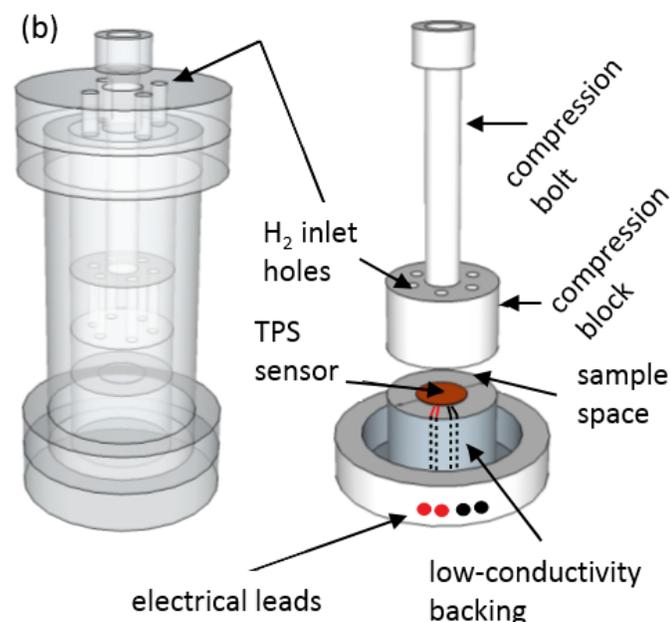


FIGURE 2. Thermal conductivity apparatus: (a) photo showing the components of the measurement apparatus and (b) schematic of a single-sided TPS measurement module

CONCLUSIONS AND FUTURE DIRECTIONS

- Efforts have continued to develop recommended volumetric capacity definitions and protocols, and these were thoroughly described in a report that will be published in a manuscript in a special edition for hydrogen storage in *Applied Physics A*.
- The hydrogen-storage community will benefit from these efforts to ensure accurate capacity measurements. Increased quality-control efforts will ensure that the proper emphasis will be placed on new hydrogen-storage materials. Recommendations addressing these issues have been made to improve measurement quality.
- We have designed and built an apparatus to measure the thermal conductivity of hydrogen storage materials over the temperature range of 77–400 K and with hydrogen over pressures up to 150 bar. The thermal conductivity apparatus is capable of measuring both pucks and powders with volumes as small as 0.5 cm³. The validation of the apparatus will begin with measurements of known materials (i.e., silica or nylon) with thermal properties similar to typical hydrogen sorption materials, as well as measurements of MOF-5 samples characterized by the Hydrogen Storage Engineering Center of Excellence. Once validated, this apparatus will be used to characterize new and existing hydrogen storage materials developed by NREL and external groups.
- The hydrogen-storage community will continue to benefit from validation efforts in the future and help ensure high quality research. NREL will continue to assist in these efforts and provide expertise for the hydrogen-storage community. NREL will expand its measurement capabilities to include variable-temperature PCT measurements. With modification to one of NREL's PCT systems and the design and construction of a cryocooler addition, NREL will be able to perform measurements between 40 K and 330 K and pressures above 160 bar. This capability will provide the opportunity to determine the energetics associated with hydrogen sorption.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Invited Paper: “*Recommended Volumetric Capacity Definitions and Protocols for Accurate, Standardized and Unambiguous Metrics for Hydrogen Storage Materials*,” P.A. Parilla, K. Gross, K.E. Hurst, T. Gennett in preparation for *Appl. Phys. A*.
2. Invited Paper: “*An International Multi-Laboratory Investigation of Hydrogen Sorbent Materials*,” K.E. Hurst, T. Gennett, P.A. Parilla, in preparation for *Appl. Phys. A*.
3. Invited Talk: “*Proposed Standard Methodologies for Hydrogen Storage Measurements on Sorbents*,” K.E. Hurst, P.A. Parilla, M. Olsen, T. Gennett, Task 32 IEA HIA Expert Meeting, January 19, 2015, Chamonix, France.

4. Talk: “*Protocols and Conventions for Volumetric Capacity Determination*,” P.A. Parilla, presentation to the Hydrogen Storage Tech Team, September 18, 2014.

5. Talk: “*Hydrogen Sorbent Measurement Qualification and Characterization*,” P.A. Parilla, DOE Materials-Based Hydrogen Storage Summit, Golden, CO January, 2015.

6. Poster: “*Hydrogen Sorbent Measurement Qualification and Characterization*,” June 2015, 2015 U.S. DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting – P.A. Parilla.

7. Poster. “*Hydrogen Sorbent Measurement Qualification and Characterization*,” July 2015, 2015 Gordon Research Conference, Hydrogen Metal Systems, Stonehill College, Easton, MA – T. Gennett.

REFERENCES

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