IV.C.1 Hydrogen Sorbent Measurement Qualification and Characterization

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- University of Missouri – Peter Pfeifer group
- National Institute of Standards and Technology, Facility for Adsorbent Characterization and Testing – ARPA-E Project
- National Institute of Standards and Technology – Laura Espinal group
- FBK, Italy – M. Testi and L. Crema
- University of South Alabama – J. Burress group

Project Start Date: October 1, 2012
Project End Date: Project continuation and direction determined annually by DOE

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.

Fiscal Year (FY) 2014 Objectives

- Develop volumetric capacity protocols and recommend their implementation to the hydrogen storage community so that material properties can be reported in a uniform and unambiguous manner.
  - Compile a complete list of volumetric capacity definitions and options needed to develop a standardized methodology to measure, calculate, interpret, and report on volumetric capacity.
  - Propose protocols for the determination of volumetric capacity of sorbent materials.
  - Submit a report that will be disseminated to the scientific community (pending at the time of this report).
- 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.

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

(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." This project focuses on this through the FY 2014 objectives as listed previously. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage material systems that meet the following 2017 DOE hydrogen storage targets:

- Cost: $12/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

The specific technical objectives include the following:

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

FY 2014 Accomplishments

- Developed recommended volumetric capacity definitions and protocols.
- Measured two external samples from outside laboratories, and we anticipate measuring two more external samples before the end of FY 2014. This surpasses the milestone of measuring three external samples.
- Collaborated with outside labs to investigate and verify operation of their hydrogen capacity equipment.
- Continued to develop realistic models for the data analysis for volumetric systems, both for isothermal and non-isothermal conditions. Used models to understand both systematic and random error sensitivities. Initiated efforts to identify these and possible other methodological/error analysis issues for differential volumetric systems. Discussed the major error sources that dominate the measurement; determined that the most dominant errors are still systematic errors. Reported detailed findings and recommendations on hydrogen capacity measurements at the International Energy Agency-Hydrogen Implementing Agreement Task 22 meeting in February 2014.
- Continued to manage and collaborate on the "Best Practices" project with its seven sections: Introduction, Capacity, Kinetics, Thermodynamics, Cycle-Life, Thermal Properties, and Mechanical Properties measurements. With the completion of the Mechanical Properties section, this will complete the Best Practice document [1].

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INTRODUCTION

The ultimate goal of the Hydrogen Storage 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. A previous round-robin study discovered major discrepancies among the different participating laboratories for capacity measurements on a standard material, both for room-temperature and liquid-nitrogen capacity determinations [2]. This study emphasizes the importance of maintaining a quality assurance effort within the hydrogen storage community. 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 volumetric capacity measurement technique; this is also known as the manometric and Sieverts technique. NREL also has extensive experience in the TPD (or thermal desorption spectroscopy) technique.

APPROACH

NREL continues with a multi-year, 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, collaborate with the hydrogen community to improve measurements, and manage and coordinate with the "Best Practices" project to disseminate recommended practices and procedures. In previous FYs, this effort was folded into the main materials-development program. This effort has its roots even before the Hydrogen Sorption Center of Excellence (HSCoE), but the effort accelerated during its existence as NREL was the main measurement resource for the HSCoE. The approach can be divided into three components: 1) work with external groups to measure samples and to examine their measurement techniques and procedures; 2) in general, analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric 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.

With respect to working with external groups, NREL actively seeks out collaborations for comparison studies, helps out 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 advise on corrective actions, if needed. This 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. In FY 2014, NREL has developed definitions and implementations for determining volumetric capacity of hydrogen storage materials. With respect to measurement error, NREL analyzes realistic models for random and systematic errors, identifies the major error sources that will dominate the measurement, and recommends improved instrumentation, protocols, and data analysis to minimize such errors.

RESULTS

1. Developed recommended volumetric capacity (VC) definitions and protocols. 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. Figures 1 and 2 give examples of how this accounting can occur for hydrogen and volumes, respectively.

   For a VC FOM that emphasizes materials, we recommend the total hydrogen capacity divided by the bulk volume of the sample. This includes all the hydrogen in the pores and adsorbed on the surface. The bulk volume is identical to the packing volume in Figure 2 with no subtraction of the skeletal volume. This material-centric FOM can be used to maximize total capacity, minimize skeletal volume, and maximize compaction-adsorption characteristics. Because this includes the free hydrogen in the pores and voids, this is also a useful engineering-centric FOM.

   For a VC FOM that emphasizes systems, we recommend the total hydrogen capacity divided by the system volume. This engineering-centric FOM includes all the hydrogen in the pores and adsorbed on the surface. The system volume includes the entire volume of materials, tanks, insulation, and balance of plant.

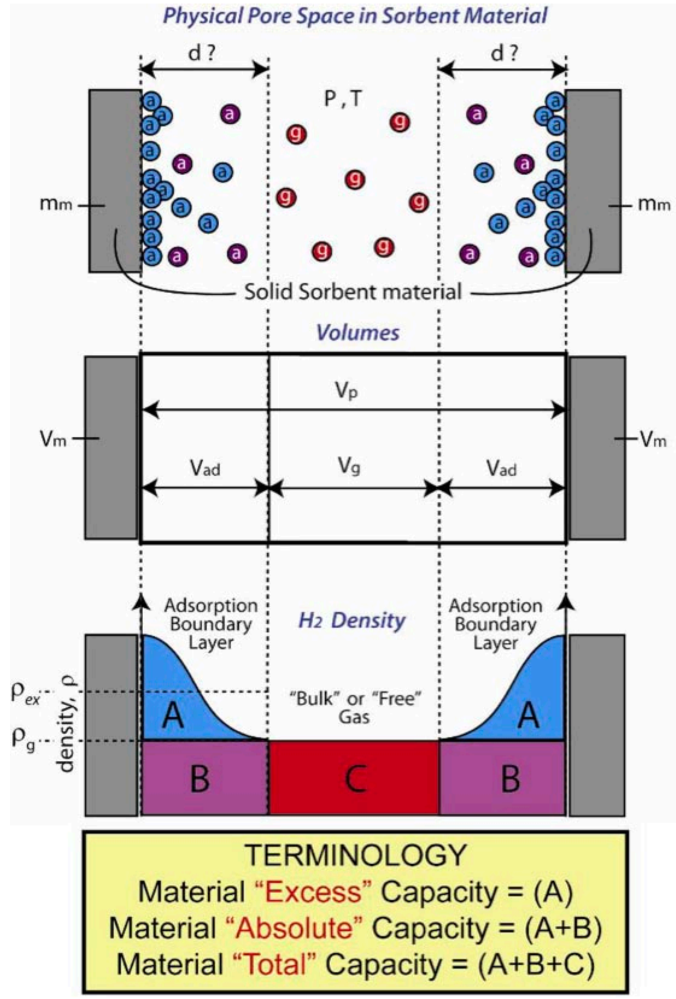

FIGURE 1. The Common Concepts Used to Label Stored Hydrogen (Figure source: adapted from Figure 81, [1])

2. Measured two external samples from other laboratories and are collaborating to have two more samples measured before the end of this FY for a total of four samples. This surpasses the milestone of measuring three external samples. Each sample undergoes approximately five measurements using different techniques in the course of a typical analysis. Techniques include multiple pressure-concentration-temperature (PCT) isotherms, Brunauer-Emmett-Teller isotherm for surface-area analysis, TPD during degas, TPD after PCT, and density and cycle-life PCT. Sample material types included high-surface-area carbons with and without catalysts, boron-substituted carbon material with and without catalysts, and metal-organic frameworks with and without catalysts. Data from these external samples are considered proprietary.

3. Collaborated with other laboratories to investigate and verify operation of their hydrogen capacity equipment. When discrepancies were found, we worked with the

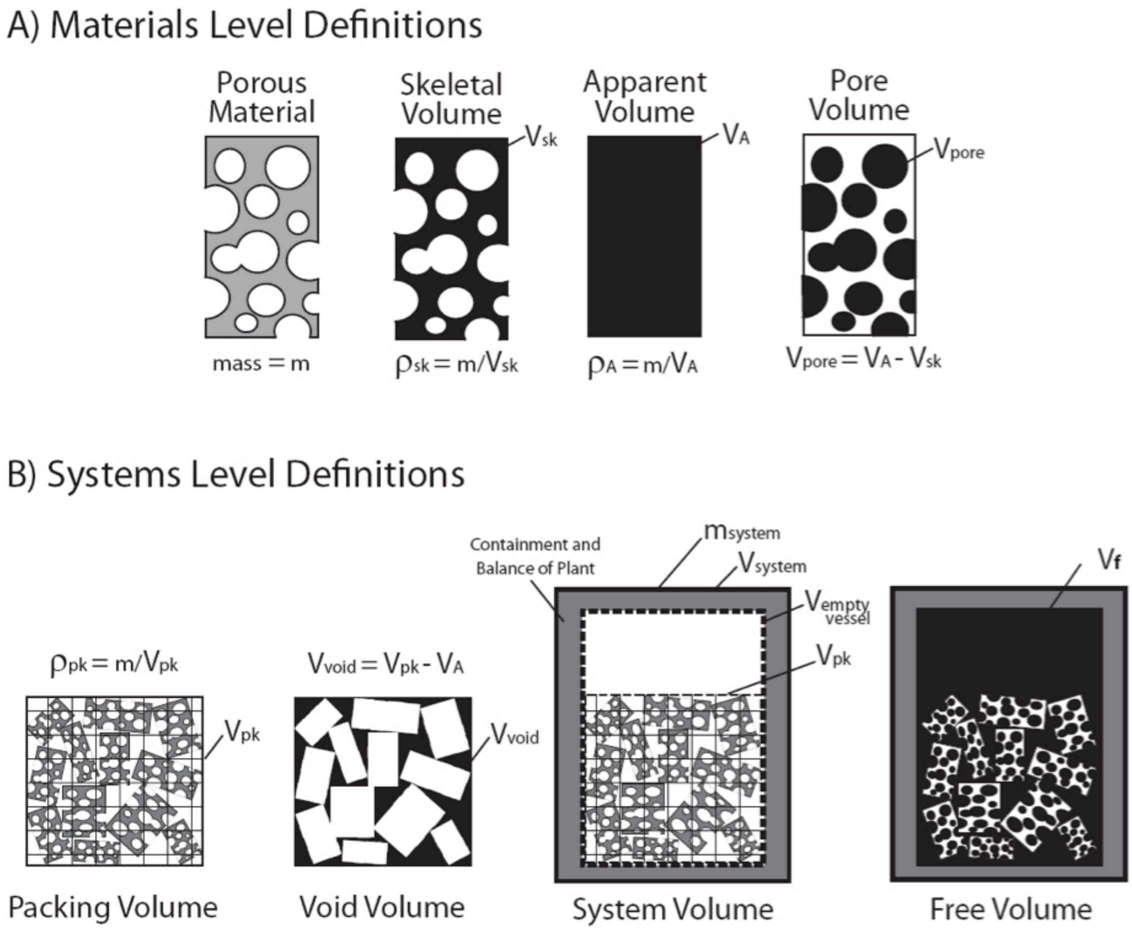

FIGURE 2. The Different Kinds of Volume Concepts and Considerations That Can Be Applied to Volumetric Capacity Definitions (Figure source: Figure 84, [1])

lab to discover the source of the discrepancy and made suggestions to remedy.

4. Continued to develop realistic models for the data analysis for volumetric 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 correct for ideal conditions, 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. Examples of real-world issues absent in the models include valves that change volume with operation and can transport gas between volumes; assumptions of non-measured pressure values; and the absence of temperature gradients or unrealistic temperature gradients. We conclude 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 acceptance of vendor number (black-box syndrome). Overall, the null calibration is the main factor in determining the accuracy of the mass-balance accounting.

CONCLUSIONS AND FUTURE DIRECTIONS

- The hydrogen storage community will benefit from efforts to ensure accurate capacity measurements. Increased quality control efforts will ensure that the proper emphasis will be placed on new hydrogen storage materials. There is sufficient cause to believe that inaccurate measurements may have misdirected emphasis.
- Direct collaboration among the laboratories performing capacity measurements has improved measurement accuracy and the quality of published results, thereby allowing for more effective utilization of the available research and development resources.

- Several key aspects of the measurement equipment and protocols have been identified to minimize experimental error. Recommendations addressing these issues have been made to improve measurement quality. We have initiated an investigation of these and possible other issues for differential volumetric systems.
- The hydrogen storage community will continue to benefit from these efforts in the future, which help ensure high-quality research. NREL will continue to assist in these efforts and provide expertise for the hydrogen storage community. NREL will adjust its measurement program to meet the needs of the DOE program, such as expanding its capabilities towards a wider range of temperatures and/or pressures or facilitating discovery of new materials.
- With the recent advances in developing prototype systems within the Hydrogen Storage Engineering Center of Excellence, it has become clear that besides hydrogen capacity (both volumetric and gravimetric) being a critical property for storage media, the thermal conductivity of these materials is also critical, as the heats of sorption/desorption must be managed within any hydrogen storage system and the material's thermal conductivity drastically affects the system design and cost. This is especially true for the sorption cycle (refueling); it is highly desirable that the refueling occur rapidly, and this exacerbates the heat removal issues. As this kind of measurement capability is uncommon, we feel the need exists to provide a facility where these measurements can occur for various types of materials, in several form factors (powder, pucks, etc.), as a function of gas pressure and sample temperature.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. "Recommended Volumetric Capacity Definitions and Protocols for Accurate and Standardized Metrics for Hydrogen Storage Materials", P.A. Parilla et al., in preparation.

2. "The Evaluation of a Multi-laboratory Analysis of the Gravimetric and Volumetric Hydrogen Sorption Properties of Sorbent Materials", K.E. Hurst, T. Gennett, P.A. Parilla, in preparation.

3. "Realistic modeling and error analysis for volumetric apparatus", P.A. Parilla et al., in preparation.

4. "Water-Mediated Cooperative Migration of Chemisorbed Hydrogen on Graphene", Y. Zhao and T. Gennett, Phys. Rev. Lett. 112, 076101 (2014).

5. Invited Talk: Task 32 IEA HIA Expert Meeting, December, 2013, Key Largo, FL – P.A. Parilla, "Protocols and Conventions for Volumetric Capacity Determination."

6. Invited Talk: June 2014, 2014 U.S. DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting – P.A. Parilla, "Hydrogen Sorbent Measurement Qualification and Characterization."

7. Talk: MRS Spring 2014 Meeting, San Francisco, CA; Symposium QQ: Computationally Enabled Discoveries in Synthesis, Structure and Properties of Nanoscale Materials – Yufeng Zhao, Thomas Gennett, "Water-Mediated Cooperative Migration of Chemisorbed Hydrogen on Graphene."

REFERENCES

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

2. Zlotea et. al., International Journal of Hydrogen Energy 34 (2009) 3044.