IV.C.11 Hydrogen Sorbent Measurement Qualification and Characterization

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Project Start Date: October 1, 2011
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2012 Objectives

- 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 temperature programmed desorption (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 Storage section of the Fuel Cell Technologies Program 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
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) 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 2012 Objectives as listed above. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE hydrogen storage targets:

- 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, 15 external samples.

FY 2012 Accomplishments

- Completed round-robin analysis of standard samples:
  - Achieved <5% error on hydrogen capacity measurements on the same standard sorbents at three different laboratories.

- Measured over 20 external samples from outside laboratories. This surpasses the milestone of measuring 15 external samples.
- Collaborated with outside labs to investigate and verify operation of their hydrogen capacity equipment.
- Developed 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.
- Identified the major error sources that dominate the measurement. We conclude that the most dominant errors are systematic errors!
- Developed recommended procedures to be used to improve measurement accuracy.
- Reported detailed findings and recommendations on hydrogen capacity measurements:
  - IEA-HIA Task 22 meeting Copenhagen, Denmark
  - DOE Fuel Cell Technologies Annual Merit Review, Washington, D.C.
  - Spillover Workshop, Winter 2012, Golden, CO
  - Summer ACS Meeting, 2011, Denver, CO
  - Spring MRS Meeting, 2011, San Francisco, CA
- Continued to manage and collaborate on the Best Practices document with its seven sections: Introduction, Capacity, Kinetics, Thermodynamics, Cycle-Life, Thermal Properties, Mechanical Properties measurements

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 the onboard hydrogen storage in hydrogen-powered vehicles. In order to develop new materials to meet these goals, it is extremely critical to accurately 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 had discovered major discrepancies among the different participating laboratories for capacity measurements on a standard material, both for room-temperature and liquid-nitrogen capacity determinations [1]. 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 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, collaborate with the hydrogen community to improve measurements, and manage and coordinate with the "Best Practices" document project to disseminate recommended practices and procedures. In previous FYs, this effort was folded into the main materials-development project. 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 two components: 1) work with external groups to measure samples and to examine their measurement techniques and procedures; and 2) in general analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric systems.

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. 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. Completed inter-laboratory comparison for spillover research project. NREL collaborated with measurement experts from six laboratories for this comparison. This was an investigation to ensure instrumentation and procedures were in agreement among the laboratories participating before the spillover study began in earnest using two types of standardized samples. Reasonable agreement among the laboratories was seen typically with less than 5% discrepancy. Figure 1 shows results

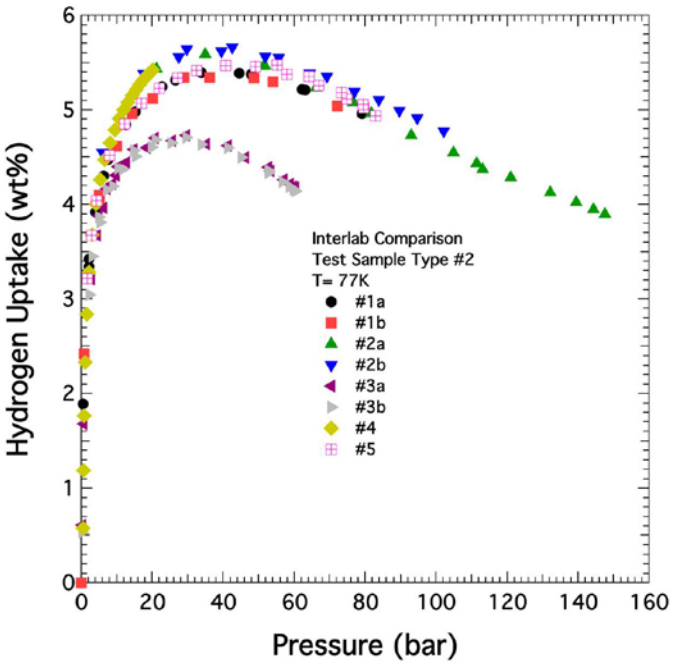

FIGURE 1. PCT data from inter-laboratory comparison study for sample type 2 at 77 K shows very good agreement among the labs except for lab #3. NREL helped Lab #3 identify measurement issues by using this material as a diagnostic tool.

for liquid nitrogen measurements for one of the standard sample types. There is one outlier lab shown in the figure (3a and 3b in the legend); this lab was not part of the main inter-laboratory comparison but was an external lab whose equipment and protocols was being diagnosed (see number 3 herein) and shows the importance of these efforts to try and improve the measurement art in the scientific community.

2. Measured over 20 external samples from outside laboratories. This surpasses the milestone of measuring 15 external samples. Each sample typically undergoes ~5 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, density and cycle-life PCT. Sample material types included templated carbon with and without catalysts, boron-substituted carbon material with and without catalysts, and metal-organic framework materials. Data from these external samples are considered proprietary and cannot be shown here.
3. Collaborated with outside labs to investigate and verify operation of their hydrogen capacity equipment. Figure 1 shows the data from one such lab (3a and 3b in the legend) and this measurement was used to help diagnose their equipment and protocols.
4. Developed 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 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. 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.
5. Identified the major error sources that dominate the measurement. We conclude that the most dominant errors are 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 ignorance of the importance of having adequate sample mass. The null calibration is the main factor in determining the accuracy of the mass-balance accounting. This can be seen in Figure 2a, which shows the total number of moles in an idealized volumetric system as a function of pressure. There are three curves, one is for an empty system, the second for the system with 100 mg of an idealized sample that adsorbs 1 wt% hydrogen (Figure 2b) at 100 bar, and the third with 1,000 mg of the same idealized sample. The null calibration is effectively equivalent to the empty curve and that “null” curve must be subtracted from the other curves to yield the adsorption results. The 100 mg curve is barely distinguishable from the null curve and shows both the importance in determining the null calibration accurately and of using an adequate sample mass as the 1,000 mg curve is easily distinguished. Error analyses performed to date include the null miscalibration, reference volume miscalibration, non-uniform temperature fluctuations, digital error, and helium adsorption during calibration.
6. Developed recommended procedures to be used to improve measurement accuracy. These include:
   - It is extremely important to measure the null calibration as accurately as possible (~1/1,000 to 1/10,000)
   - The system should be tested (and occasionally retested) with no sample to determine its ability to measure ‘zero’ adsorption (isothermal and non-isothermal conditions)
   - The system should be tested with a known material to check the absolute calibration

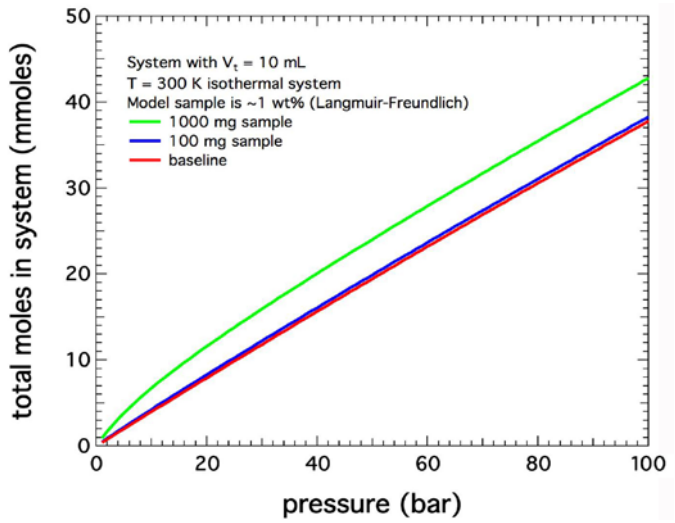

FIGURE 2A. Model data for an idealized 10 mL volumetric measurement system shows the number of total moles in the system as a function of pressure. The three curves show the number of moles with no sample (red), 100 mg of an idealized 1 wt% sample (blue) and 1,000 mg of the same sample (green). This shows the importance of accurately calibrating the system and having adequate sample mass as the red and blue curve are barely distinguishable (see text for discussion).

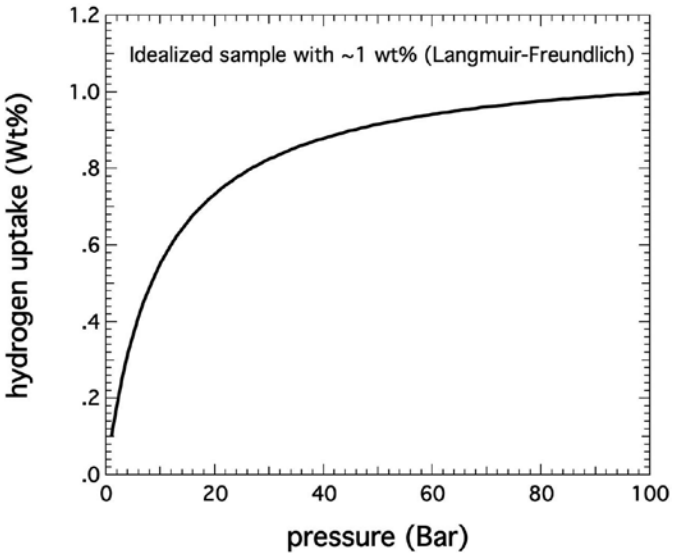

FIGURE 2B. Model sample data used for the example of Figure 2a shows an idealized sample material with 1 wt% hydrogen adsorption at ~100 bar.

  - The system's temperature profile should be controlled and monitored (pressure stability test)
  - Use the highest sample mass as possible for measurements

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.
- The hydrogen-storage community will continue to benefit from these 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 adjust its measurement program to meet the needs for the DOE program, such as expanding its capabilities towards a wider range of temperature and/or pressure or facilitating new materials.

Special Recognitions & Awards/Patents Issued

1. NREL Team of the Month (November, 2011) - Katherine Hurst, Jeffrey Blackburn, and Philip Parilla, for One Time Special Effort related to hydrogen storage work.

FY 2012 Publications/Presentations

1. Two papers submitted: 1 on volumetric measurements; 1 on TPD calibration:

  - "Critical and precise calibration required to avoid large systematic errors in volumetric apparatus: isothermal case" *submitted to Review of Scientific Instruments, P.A. Parilla et al.*
  - *"A Dynamic Calibration Technique for Temperature Programmed Desorption Spectroscopy" submitted to Review of Scientific Instruments, K.E. Hurst et al.*

2. Two papers in preparation on volumetric measurements focusing on proper modeling, error analysis and methodology:

  - "Realistic modeling and error analysis for non-isothermal volumetric apparatus" *in preparation, P.A. Parilla et al.*
  - "Modeling and error analysis for a differential Sieverts apparatus" *in preparation, P.A. Parilla et al.*

3. One paper published in JACS by Northwestern University:

  - "Designing Higher Surface Area Metal–Organic Frameworks: Are Triple Bonds Better Than Phenyls?", *Farha, Omar; Wilmer, Christopher; Eryazici, Ibrahim;*

Hauser, Brad; O'Neill, Kevin; Parilla, Philip; Sarjeant, Amy; Nguyen, SonBinh; Snurr, Randall; Hupp, Joseph; J. Am. Chem. Soc., **2012**, 134 (24), pp 9860–9863

4. Invited Talk Spring 2011 MRS – P.A. Parilla: *"Round-Robin Results on Measuring Materials For Hydrogen Storage and Critical Calibration Issues"*

5. Invited Talk Summer 2011 ACS – P.A. Parilla: *"Common Errors Found In Volumetric Hydrogen Capacity Measurements And How To Avoid Them"*

6. Invited Talk Fall 2011 IHA – P.A. Parilla: *"Improving the reproducibility and uptake kinetics of chemisorptive (spillover) materials" (This talk had substantial content on the round-robin results and measurement issues and errors.)*

7. Talk at Spillover Workshop Winter 2012: *"Inter-Laboratory Comparison: Testing Measurement Reproducibility and Accuracy"*

References

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