IV.C.1 Hydrogen Sorbent Measurement Qualification and Characterization

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- National Institute of Standards and Technology, Facility for Adsorbent Characterization and Testing (FACT) – ARPA-E Project
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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.
- Assist research groups within the hydrogen storage community to perform robust and accurate measurements of the 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) 2013 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 TPD systems:
  - Analyze *realistic* models for random and systematic errors.
  - Develop ad hoc working standards to assist in diagnosing and testing hydrogen capacity measurement instrumentation.
  - 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 2013 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:

- Cost: $4/kWh net
- Specific energy: 1.5 kWh/kg

- Energy density: 0.9 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 2013 Accomplishments

- Developed an ad hoc working standard of an activated-carbon material to test instrumentation and measurement protocols for hydrogen capacity.
- Measured three external samples from outside laboratories. This surpasses the milestone of measuring two 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.
- Discussed the major error sources that dominate the measurement; the most dominant errors are still systematic errors.
- Reported detailed findings and recommendations on hydrogen capacity measurements.
- 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.

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 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 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" 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, but the effort accelerated during its existence as NREL was the main measurement resource for the Hydrogen Sorption Center of Excellence. 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. In this FY, NREL has looked at several commercially available activated carbons to be used as standardized samples. 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 an ad hoc working standard of an activated-carbon material to test instrumentation and measurement protocols for hydrogen capacity. This standard will be for both room temperature and liquid-nitrogen temperature measurements. The room-temperature work has been completed and the liquid-nitrogen work is still progressing at the time of this report. It is expected that the latter will be completed by September 2013. Five activated carbons were obtained from well-known commercial chemical supply companies and each went through a series of tests to determine their suitability as a standard material. Some of the criteria that are desirable for a standard material are: 1) commercially available, 2) easily handled, 3) non-hazardous, 4) little or no contaminants, 5) a reasonable hydrogen capacity but not too easy, 6) reproducible results, 7) air stable, 8) long shelf life, and 9) degassing protocol should be reasonable and not extreme. During an initial degassing procedure, it became apparent that several samples contained impurities that are commonly associated with activated carbons: sulfur. Both Brunauer-Emmett-Teller (BET) and pressure-concentration-temperature (PCT) measurements were performed. Figure 1 shows the PCT results for a survey of five different activated carbon samples in the initial screening to find the standardized material. Sample #2 showed the best PCT isotherm, had a reasonable BET value (1,234 m^2/g), and had no detectable impurities; therefore, it is the leading candidate for the standard material.

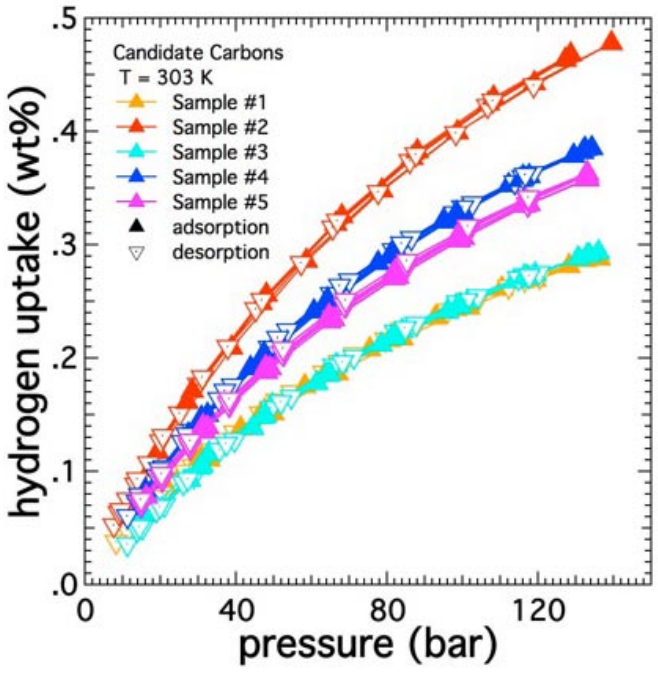

FIGURE 1. PCT measurements (hydrogen capacity versus pressure) to find an ad hoc standard sample for room temperature measurements. Sample #2 has the highest capacity among the materials examined.

2. Measured three external samples from outside laboratories. This surpasses the milestone of measuring two external samples. Each sample typically undergoes approximately five measurements using different techniques in the course of a typical analysis. Techniques include multiple PCT isotherms, BET, TPD during degas, TPD after PCT, density and cycle-life PCT. Sample material types included templated carbon with and without catalysts, BC_x (a boron substituted carbon material formed by the pyrolization of triethylborane) with and without catalysts, and metal-organic frameworks. 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. When discrepancies were found, we worked with the lab to discover source of the discrepancy and made suggestions to remedy it.
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 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. 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. An example of the importance of the null calibration constant is demonstrated in Figure 2. It shows several PCT curves that all come from the same raw data but use different null calibration constants to calculate the hydrogen capacity; the black curve is the correct data. This clearly demonstrates how important it is to determine the correct null calibration constant. How sensitive the influence of an error in the null calibration is on the resulting PCT data depends on several factors,

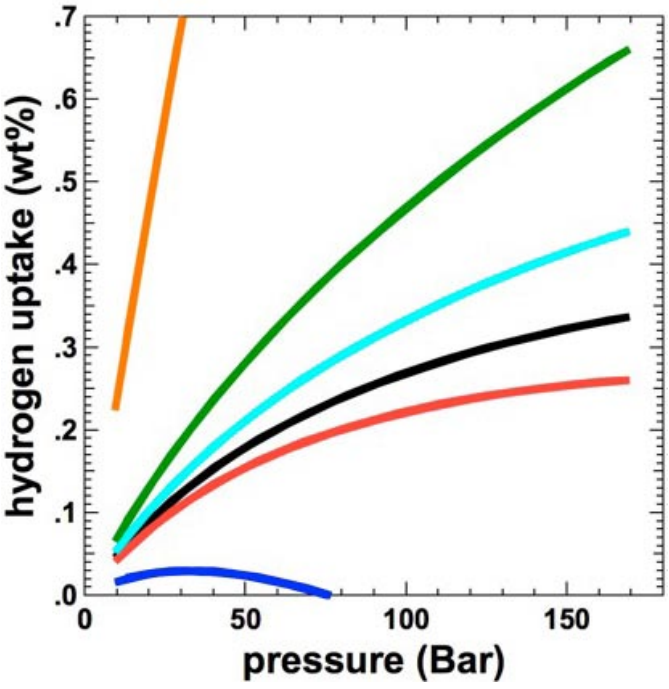

FIGURE 2. PCT curves that all come from the same raw data, but use different null calibration constants to calculate the hydrogen capacity; the black curve is the correct data. This clearly demonstrates how important it is to determine the correct null calibration constant.

but the most important are: the magnitude of the error, the specific capacity of the sample and the mass of the sample.

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. An ad hoc standard material will facilitate in determining proper instrument calibration and measurement protocols.
- 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.
- With the recent advances in developing prototype systems within the Hydrogen Storage Engineering Center of Excellence, it has become clear that hydrogen capacities based on a volumetric basis are equally, if not more, important for material comparison. Since previously this reporting practice has not been as emphasized, there is perhaps even more ambiguity and confusion regarding the proper measurement procedures, data analysis and reporting for the volumetric capacities of materials. We feel the need exists to explore and discuss the various options within the hydrogen storage community, both domestically and internationally.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. 2013 DOE Hydrogen and Fuel Cell Program R&D Award, "In recognition of outstanding achievements in the establishment of best practices for characterizing hydrogen storage materials", awarded to Karl Gross ("Best Practices" document) and Philip Parilla (NREL measurement science efforts and technical monitor for "Best Practices").

FY 2013 PUBLICATIONS/PRESENTATIONS

1. "A dynamic calibration technique for temperature programmed desorption spectroscopy", Hurst, K.E., Heben, M.J., Blackburn, J.L., Gennett, T., Dillon, A.C., Parilla, P.A., Review of Scientific Instruments **84** 025103 (2013).

2. "Realistic modeling and error analysis for non-isothermal volumetric apparatus" in preparation, P.A. Parilla et al.

3. "Modeling and error analysis for a differential Sieverts apparatus" in preparation, P.A. Parilla et al.

4. Invited Talk Oct. 2012, FACT Meeting– P.A. Parilla *"Lessons Learned from the DOE Hydrogen Program: Adsorption Measurements."*

5. Invited Talk May 2013, 2013 U.S. DOE Hydrogen And Fuel Cells Program Annual Merit Review And Peer Evaluation Meeting – P.A. Parilla *"Hydrogen Sorbent Measurement Qualification and Characterization."*

REFERENCES

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