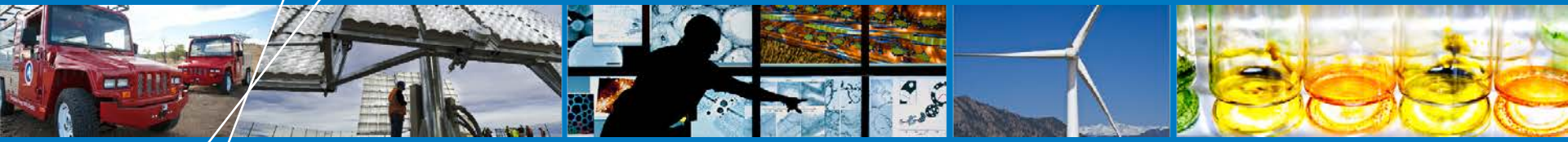
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Hydrogen Sorbent Measurement Qualification and Characterization



2012 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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ST014

May 16, 2012

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline*

Start: October 2011
End: September 2012
% complete: ~50%

*previously a component of NREL's materials development program and supported annually since 2006

Budget FY 12

Funding 2012
$200,000

(Funding 2011 $180,000)

Barriers addressed

General: A. Cost, B. Weight and Volume,
C. Efficiency, E. Refueling Time
Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Collaborators

Caltech, USA – Channing Ahn group

H2Technology Consulting, USA – Karl Gross

Institut de Chimie et des Matériaux, France – Claudia Zlotea

Max Planck, Germany – Michael Hirscher group

Northwestern University, USA – Joe Hupp group

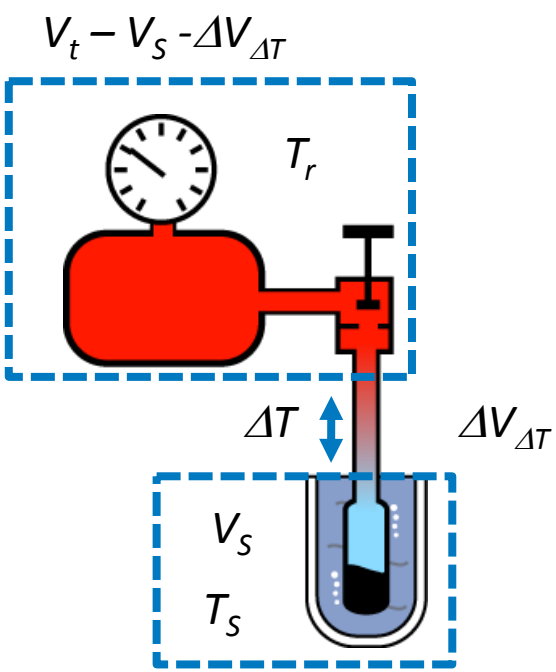
Penn State, USA – Angela Lueking group

SwRI®, USA – Mike Miller

Relevance: Measurement Validation

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



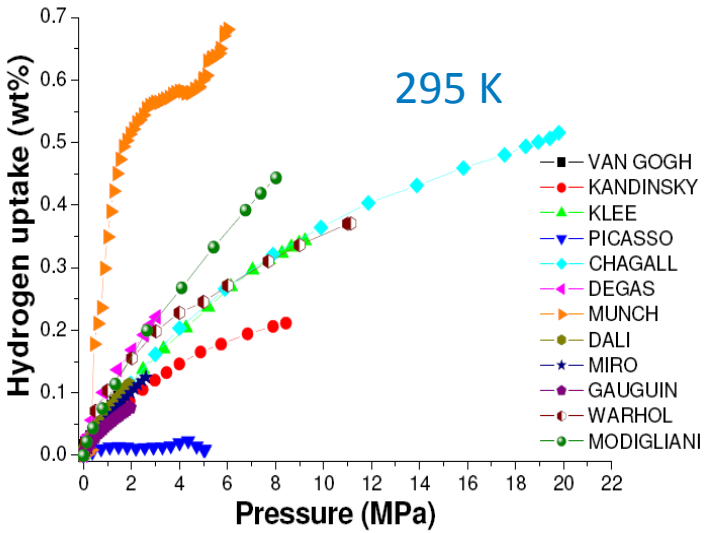
Manometric (aka Volumetric) System

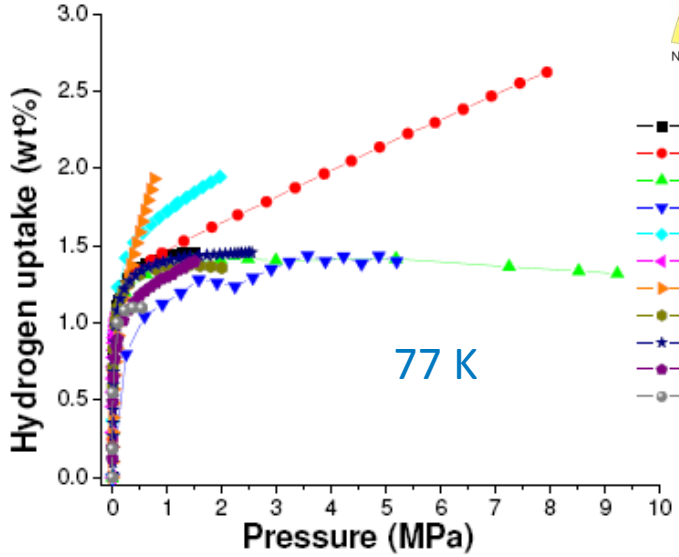
Project Goal:

- 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 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

Relevance: Previous Round-Robin Testing Show Alarming Inter-Laboratory Scatter

NESSHY Round-Robin Testing Results for High Surface Area Material





Remarkable scatter among participating laboratories, emphasizing the need to review methods and internal calibration or operability of analytical equipment

What is going on?

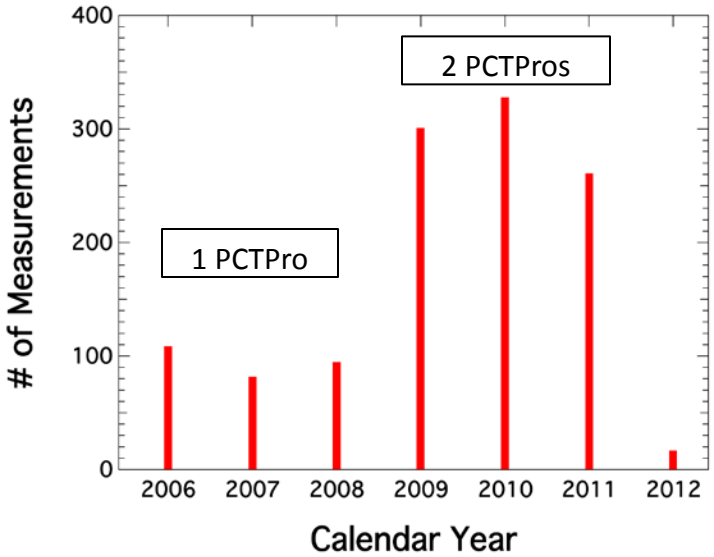
Systematic Error!

Zlotea et. al., International Journal of hydrogen energy 34 (2009) 3044 – 3057; Miller, SWRI

Approach: Continuation of Multi-Year Effort

- **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
  - Manage & coordinate with the "Best Practices" Project (ST052 - Karl Gross) to disseminate recommended practices and procedures

# of High-Pressure Measurements*



~1200 High-Pressure Measurements Since 2006

- **In previous FYs, this effort was folded into the main materials-development program and was not separately reviewed.**
- **This effort has its roots even before the Hydrogen Sorption Center of Excellence (HSCoE), but the effort accelerated during the HSCoE as NREL was the main measurement resource for the HSCoE.**

*Measurements include H_2 capacity, life-cycle, He calibrations at room and LN_2 temperatures, instrument calibration and testing, methodology development and testing

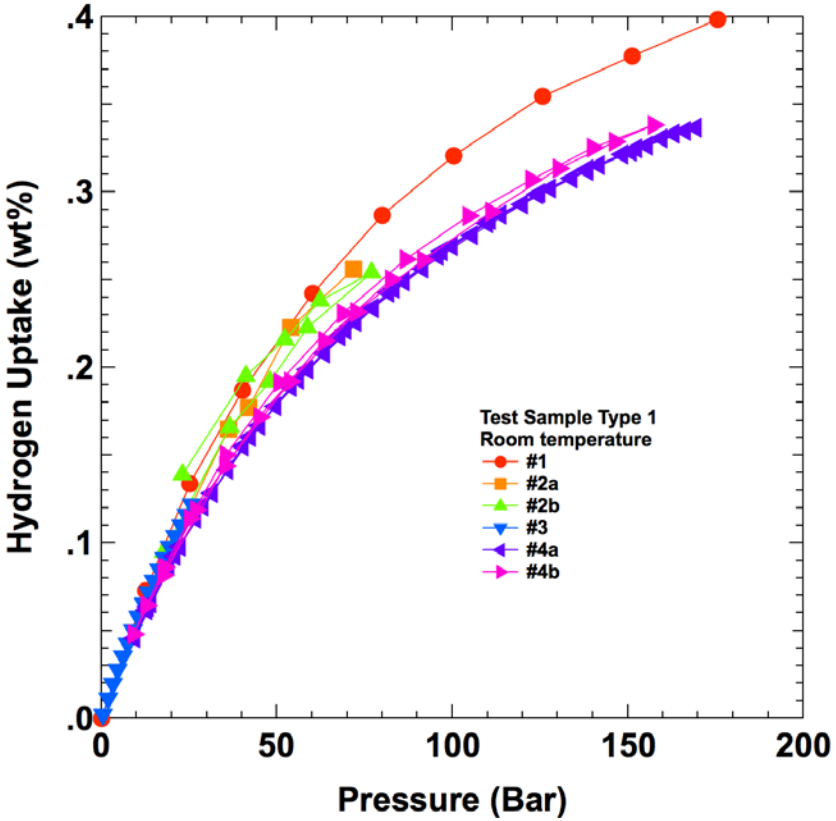
Approach: Work with external groups to measure samples and to examine measurement techniques and procedures

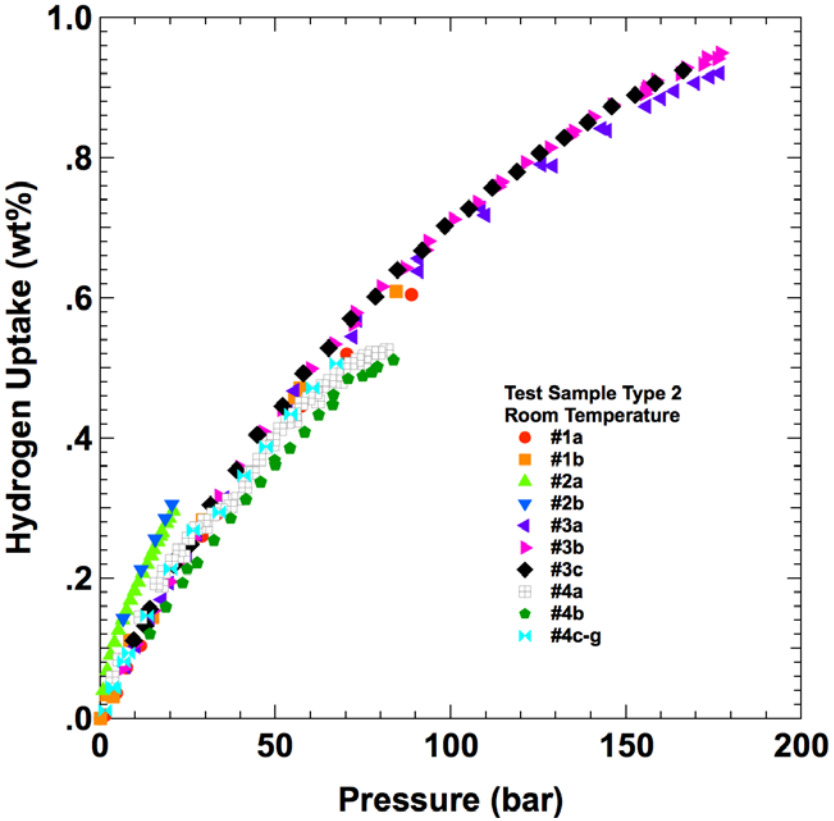
- **Measure external samples at NREL to compare results with source group's and/or third-party's results**
  - Actively seek out collaborations for comparison studies
  - Help out with DOE projects to ensure robust measurements
  - Test very promising results for verification
- **Discover sources of measurement discrepancies and advise on corrective actions, if needed, for source group**
  - Send standardized samples to external labs to test instrumentation and experimental procedures
  - Examine data and data analysis protocols to discover possible avenues to improve measurement techniques
  - Make recommendations to labs for improvement

Accomplishments & Progress: Inter-Laboratory Comparison for Spillover Research (ST021)

Investigation to ensure instrumentation and procedures were in agreement among the laboratories participating in the spillover study using two types of standardized samples

Reasonable agreement is generally seen



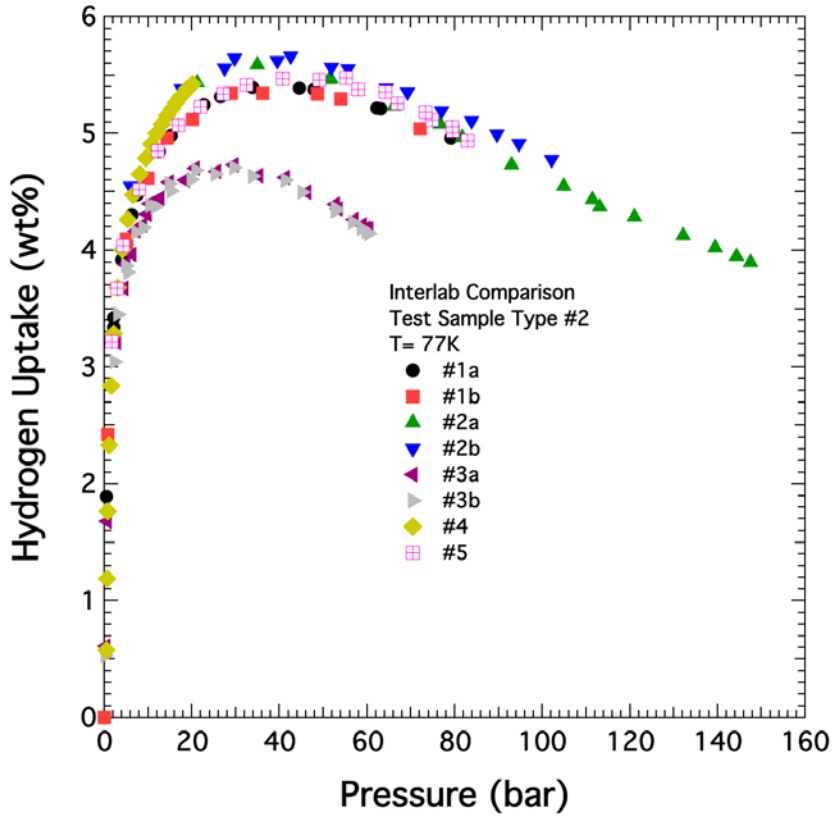


Results for test samples at room temperature

Accomplishments & Progress: Measurements of External Samples & Collaboration with External Labs for Measurement Protocols

- **20 external samples have been processed to date**
- **This represents ~100 measurements**
- **Data is considered proprietary and cannot be shown here**
- **Measurements include**
  - Multiple PCT isotherms
  - BET
  - TPD during degas
  - TPD after PCT
  - Density
  - Cyclability

PCT data using a standard material at 77K is plotted below. NREL helped an external lab (#3) diagnose their PCT system with this test.

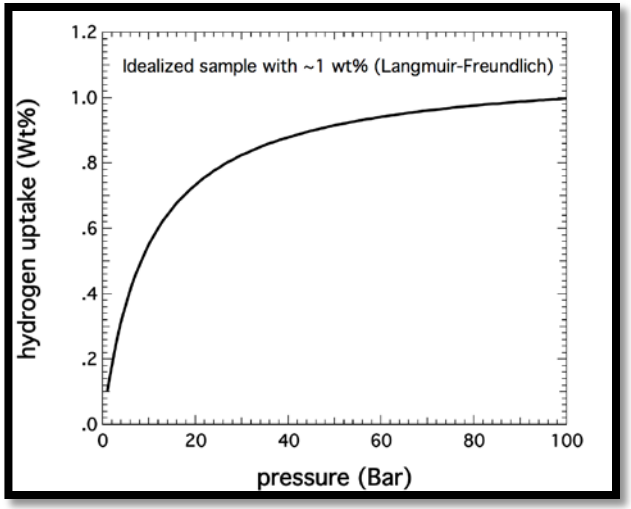


Approach: Analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric systems

- **Analyze *realistic* models for random and systematic errors**
  - 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:
    - Valves that change volume with operation and can transport gas between volumes
    - Assumptions of non-measured pressure values
    - Absence of temperature gradients or unrealistic temperature gradients
- **Identify the major error sources that will dominate the measurement**
  - The most dominant errors are systematic errors!
  - Sources of systematic error:
    - Improper "null" calibration
    - Inadequate data analysis models (mass-balance models)
    - Ignorance of the large error associated with non-uniform temperature fluctuations
    - Ignorance of the importance of having adequate sample mass
- **Recommend improved instrumentation, protocols and data analysis to minimize such errors**
  - NREL emphasizes the need for careful procedures and control experiments
  - NREL manages and collaborates on the "Best Practices" project (ST052)

Accomplishments & Progress: Realistic Mass-Balance Models

- **Realistic model takes into account:**
  - No assumptions needed for unmeasured pressures
  - Valves' behavior accounted for
  - Accurate accounting for temperature profile

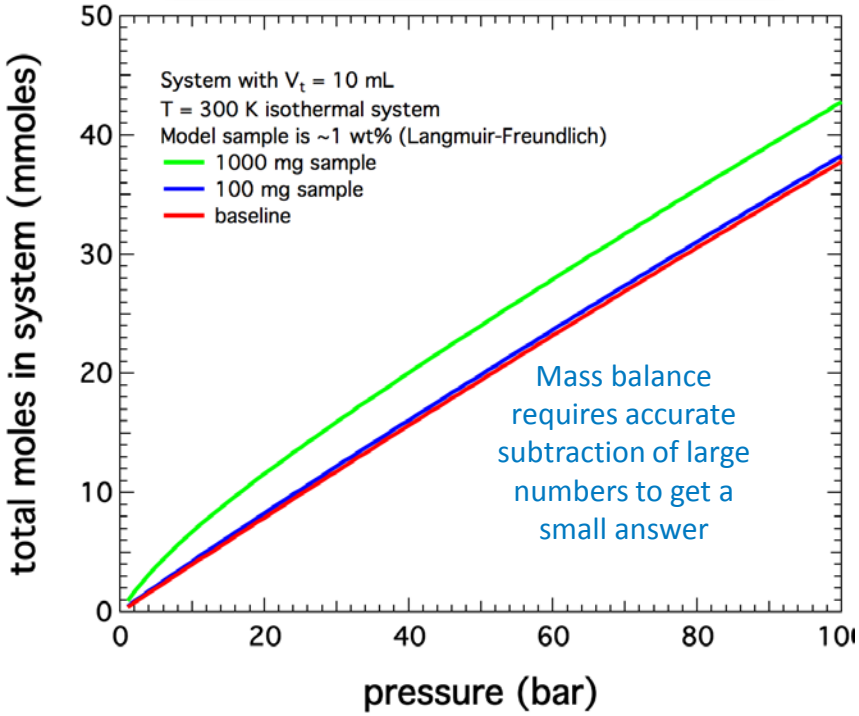


Equation for isothermal system

$$n_{ads_i} = \left(\frac{V_r}{RT}\right)\left[\left(\frac{P_{Ch_i}}{z_{Ch_i}} - \frac{P_{Cl_i}}{z_{Cl_i}}\right) - \gamma\left(\frac{P_{Eq_i}}{z_{Eq_i}} - \frac{P_{Eq_{i-1}}}{z_{Eq_{i-1}}}\right)\right]$$

$$z_{S_i} = z_{gas}(P_{S_i}, T); \qquad \gamma = V_t / V_r$$

Moles adsorbed on the ith step

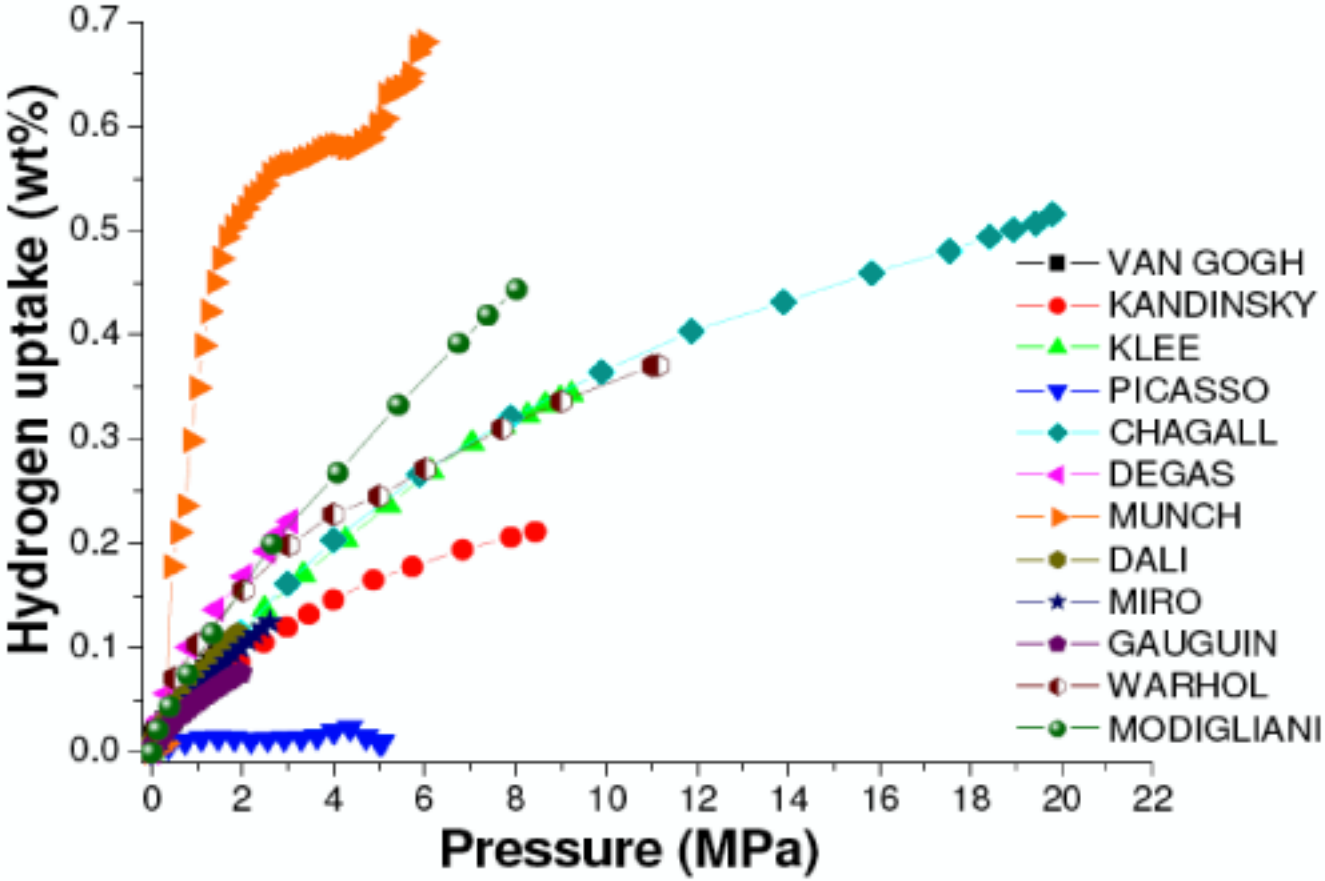


Accomplishments & Progress: Thorough Error Analysis and Recommended Procedures

- **Error Analysis on Full Mass-Balance Model:**
  - Null miscalibration
  - Reference volume miscalibration
  - Non-uniform temperature fluctuations
  - Digital error
  - Helium Adsorption during calibration
- **Recommended Procedures:**
  - It is extremely important to measure the null calibration as accurately as possible (~ 1 /1000 to 1/10,000)
  - The system should be tested (& 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
  - The system's temperature profile should be controlled and monitored (pressure stability test)
  - Use the highest sample mass as possible for measurements

Effect of Changing Null Calibration

All these curves are from the same raw data but with different null calibrations constants



urve has “correct” null calibration

This slide has animation effects; see Technical Back-up Slides

Accomplishments & Progress: Milestones & Deliverables

- **Milestone: "Provide summary of measures on 15 external samples" (April, 2012)**
  - 20 samples measured to date (March, 2012)
  - Report pending, milestone is 100% complete
- **Deliverable: "Disseminate measurements qualification and validation improvements to the hydrogen community"**
  - Invited Talk Spring 2011 MRS
    "Round-Robin Results on Measuring Materials For Hydrogen Storage and Critical Calibration Issues"
  - Invited Talk Summer 2011 ACS
    "Common Errors Found In Volumetric Hydrogen Capacity Measurements And How To Avoid Them"
  - Invited Talk Fall 2011 IHA
    "Improving the reproducibility and uptake kinetics of chemisorptive (spillover) materials"
  - Talk at Spillover Workshop Winter 2012
    "Inter-Laboratory Comparison: Testing Measurement Reproducibility and Accuracy"
  - 3 Papers in preparation (2) or submitted (1) on volumetric measurements focusing on proper modeling, error analysis and methodology
  - 1 Paper submitted on temperature programmed desorption (TPD) calibration techniques

Collaborations

Activities include: technical discussions on equipment and procedures, sample exchange, & data analysis

- Caltech, USA – Channing Ahn group
- H2Technology Consulting, USA – Karl Gross
- Institut de Chimie et des Matériaux, France – Claudia Zlotea
- Max Planck, Germany – Michael Hirscher group
- Northwestern University, USA – Joe Hupp group
- Penn State, USA – Angela Lueking group
- SwRI®, USA – Mike Miller

Proposed Future Work

- **Continue FY12 efforts to measure external samples, assist others in improving measurement procedures, hold a measurement workshop, publish error analysis and recommended protocols**
- **Coordinate with new projects and DOE to ascertain new measurement needs and improve NREL's capabilities to meet those needs**
  - Liquid-based sorbents
  - New temperature ranges
  - Higher pressure systems (~400 bar)
- **Add new capabilities to community efforts**
  - Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
  - High pressure NMR

Summary

- **Relevance: Measurement Validation**
  - Determining which materials are promising for hydrogen storage is crucial
  - Implement proper measurement techniques and procedures
- **Approach**
  - Identify, implement and disseminate corrective measures for sources of error in volumetric systems
  - Verify measurements on external samples
- **Accomplishments & Progress**
  - Developed realistic models, identified major sources of errors, disseminated improvement through talks and publications
  - Have measured 20 external samples (to date); 15 was the milestone
- **Collaborations**
  - Interacted with 7 groups on measurement techniques and procedures
  - Measured samples from 6 external groups
- **Proposed Future Work**
  - Develop new capabilities to meet future measurement requirements such as higher pressure, liquid-based systems, and wider temperature ranges

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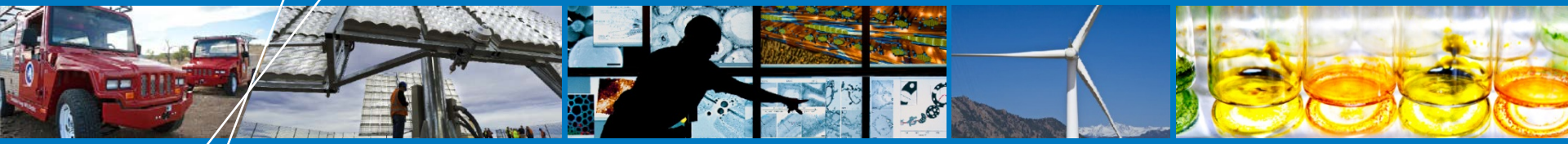
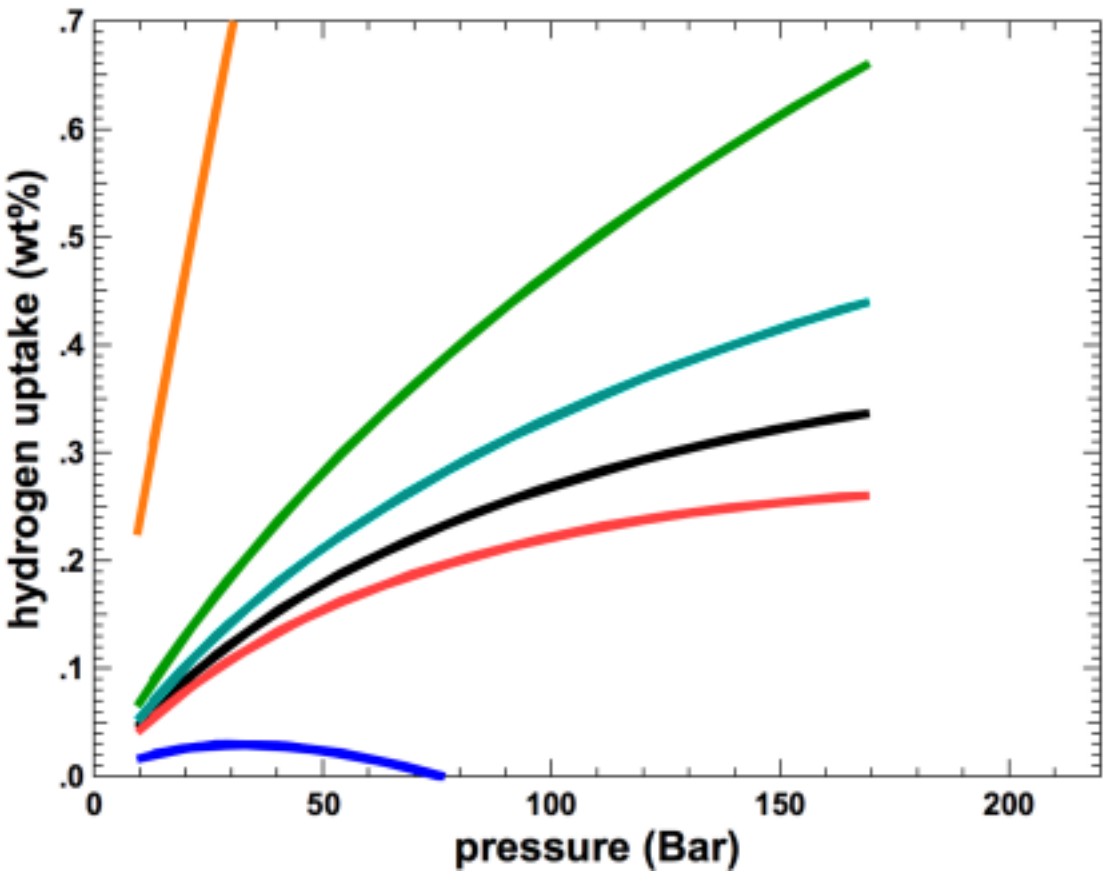


Technical Back-Up Slides

Effect of Changing Null Calibration

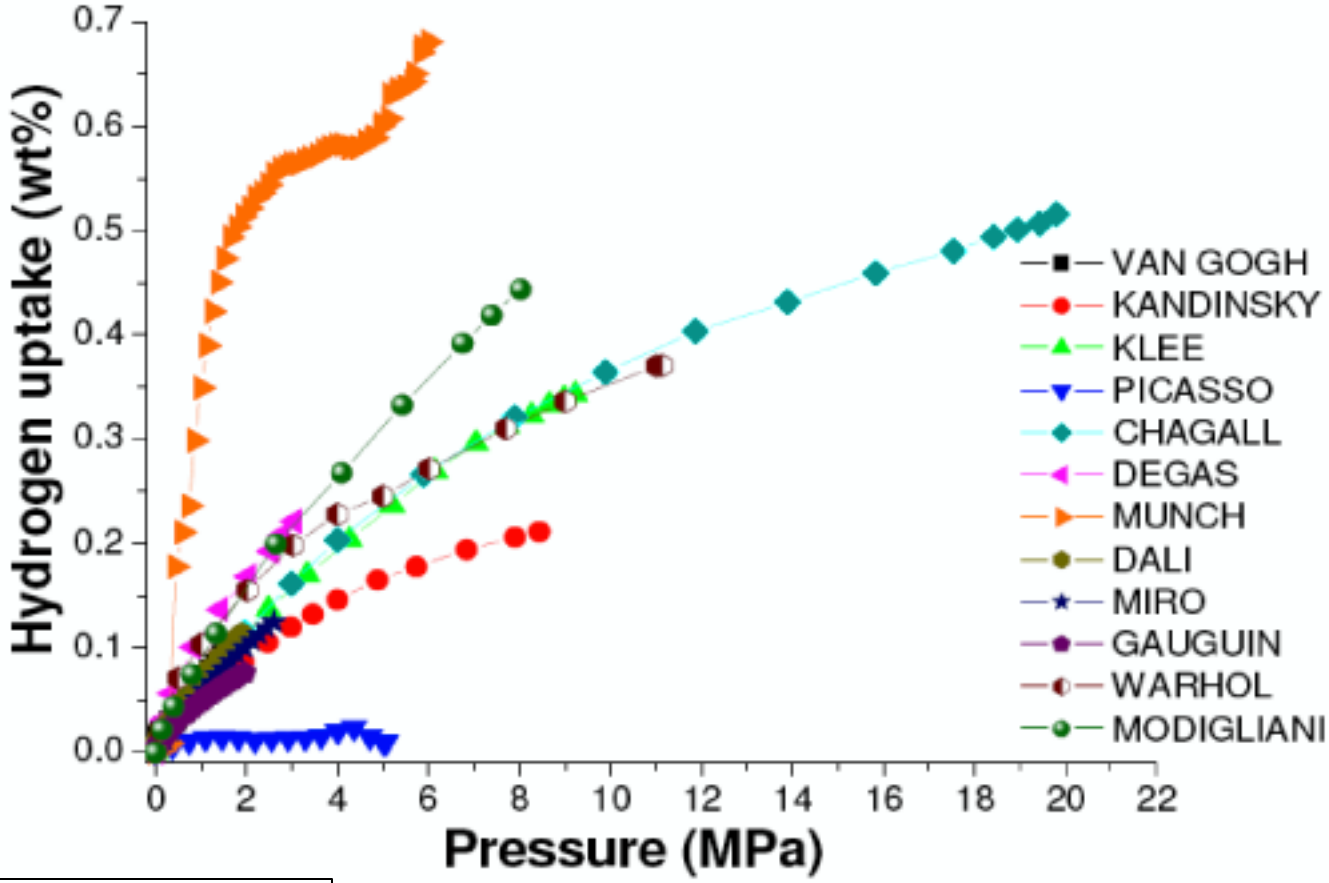
- **All these curves are from the same raw data but with different null calibrations constants**



Black curve has "correct" null calibration

First slide of animation

Effect of Changing Null Calibration



Last slide of animation

Non-Isothermal Measurements

Models have been developed to realistically handle non-isothermal measurements.

Equation must reflect the volumes at different temperatures and the temperature gradient

$$n_{ads_i} = \frac{1}{R\,T_r}\left[\left(\frac{P_{Chr_i}}{z_{Chr_i}} - \frac{P_{Clr_i}}{z_{Clr_i}}\right)V_r - \left(\frac{P_{E_i}}{z_{Er_i}} - \frac{P_{E_{i-1}}}{z_{Er_{i-1}}}\right)\left(V_t - V_s - \Delta V_{\Delta T}\right)\right]$$

$$- \frac{V_s}{R\,T_s}\left(\frac{P_{E_i}}{z_{Es_i}} - \frac{P_{E_{i-1}}}{z_{Es_{i-1}}}\right) - \frac{\Delta V_{\Delta T}}{R}\left(\frac{P_{E_i}}{\tau_{E_i}} - \frac{P_{E_{i-1}}}{\tau_{E_{i-1}}}\right)$$

$$z_{Xk_i} \equiv z\left(P_{X_i}, T_k\right) \quad ; \quad \frac{1}{\tau_{E_i}} \equiv \frac{1}{L}\int_{x=T_r}^{x=T_s} \frac{dx}{T(x)\,z(P_{E_i}, T(x))}$$

Why is accuracy so important?

- **Inaccurate measurements create confusion in the research community (false positives & false negatives)**
- **Wastes time & money for all involved**
  - Originating group
  - Funding agency
  - Other research groups who try and replicate the results
  - Misdirects funding to poor materials
  - Prematurely dismisses a promising material
- **Damages reputations**

Interpretation of Null Calibration Error

- **If error in γ is $\Delta\gamma$, then this can be expressed as an error in V_t, ($\Delta V_t = V_r \ \Delta\gamma$), then the <u>accumulated</u> contribution to the sample adsorption error be expressed as:**

$$\Delta n_{ads\,err} = \frac{P\,\Delta V_t}{R\,T\,z(P,T)}$$

…just the amount of gas in ΔV_t at P and T. ***This is an absolute error unrelated to the sample!!!***

- **This confirms that, besides efforts to minimize ΔV_t, the sample mass must be maximized**
- **How careful must one be?**

γ calibration needs 0.1% to 0.01% relative error!

➔ ***very careful calibration required!***