

Weak Chemisorption Validation



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National Renewable Energy
Laboratory (NREL)

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2011 DOE Hydrogen and Fuel
Cells Program Review

ST021

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

Start: October 2010
End: September 2011
% complete: ~50%

Budget FY 11

Funding 2011

\$585k*

* \$225k committed to the 4 subcontracts

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

Partners (PI)

University of Hawaii - Craig M. Jensen,

University of New Mexico - Plamen Atanassov

Max Planck, Stuttgart, Germany - Michael
Hirscher

**Institut de Chimie et des Matériaux – Paris,
France** - Michel Latroche.

Collaborators: *LANL - Tony Burrell; Penn State -
Angela Lueking; Griffith University - Evan Gray; Curtin
University - Craig Buckley*

Relevance:

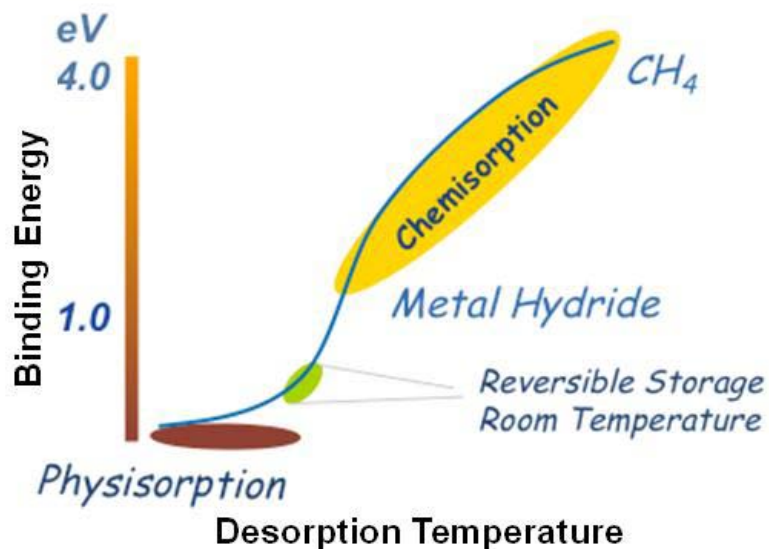
DOE Objective:

Evaluate the spillover process as a means to achieve DOE 2015 Hydrogen Storage goals.

Project Goal:

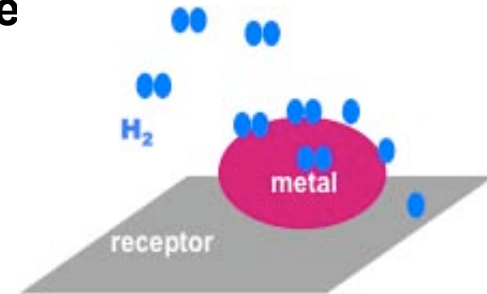
- Validation of measurement methods.
 - Reproducibility
 - Round-robin measurements of standards at several sites
- Identification and synthesis of several candidate sorbents for spillover.
- Determination of hydrogen sorption capacity enhancement from spillover.
- Observation and characterization of spillover hydrogen-substrate interactions with spectroscopic techniques.

Binding Energy and Sorption-Desorption



Hydrogen Spillover for Hydrogen Storage

- **Catalytic dissociation of H₂ and transfer to a substrate**
 - carbon, metal oxide, MOF, etc.
- **Spillover well-documented for catalytic processes.**
- **Key issues**
 - Nature of the binding of H to substrate.
 - Kinetics of hydrogen diffusion (H mass transport on/in substrate).
 - Extent of enhancement of storage capacity relative to simple molecular H₂ physisorption.
 - How to maximize hydrogen storage capacity through spillover.
 - Extent of activation of sorbent/catalyst upon hydrogen spillover.
- **Key Conclusions from CoE**
 - Chemical potential of catalyst rises with hydrogen saturation, to permit spillover onto receptor.*
 - Inter-phase diffusion of adsorbed hydrogen (pores).
 - Recombination for desorption is not currently thought to be rate limiting.
 - Limited reproducibility of spillover material maximum sorption capacities.



*Hansong Cheng, Liang Chen, Alan C. Cooper, Xianwei Sha and Guido P. Pez, *Hydrogen spillover in the context of hydrogen storage using solid-state materials* *Energy Environ. Sci.*, 2008, 1, 338-354

Abhishek K. Singh, Morgana A. Ribas and Boris I. Yakobson, *H-Spillover through the Catalyst Saturation: An Ab Initio Thermodynamics Study* *ACS Nano*, 2009, 3 (7), pp 1657-1662

Kyuhoo Lee, Yong-Hyun Kim, Y. Y. Sun, D. West, Yufeng Zhao, Zhongfang Chen, and S. B. Zhang, *Hole-Mediated Hydrogen Spillover Mechanism in Metal-Organic Frameworks*, *Phys. Rev. Lett.* 104, 236101 (2010)

Approach: Workshop Summary. Utilized expertise across all three previous DOE CoEs and IEA-HIA Task 22 (August 2010)

Objective:

- Universal reproducibility of enhanced adsorption spillover effects.
- Establish if spillover is a viable process for hydrogen storage.

Approach:

- Validate observations for a narrow range of spillover material systems with at least 15% hydrogen sorption enhancement. (No new materials discovery.)
- Synthesize and distribute targeted materials for group analysis.
- Spectroscopic characterization, IR (DRIFTS), NMR and Neutron Scattering.
- Incorporate new information within mechanistic models.

Goals:

- Ascertain H/H₂-catalyst-substrate interactions and mechanisms.
- Establish reproducibility of synthesis and validity of measurements.
- Establish whether DOE targets can be reached.
- Communication of validated results to community at large.

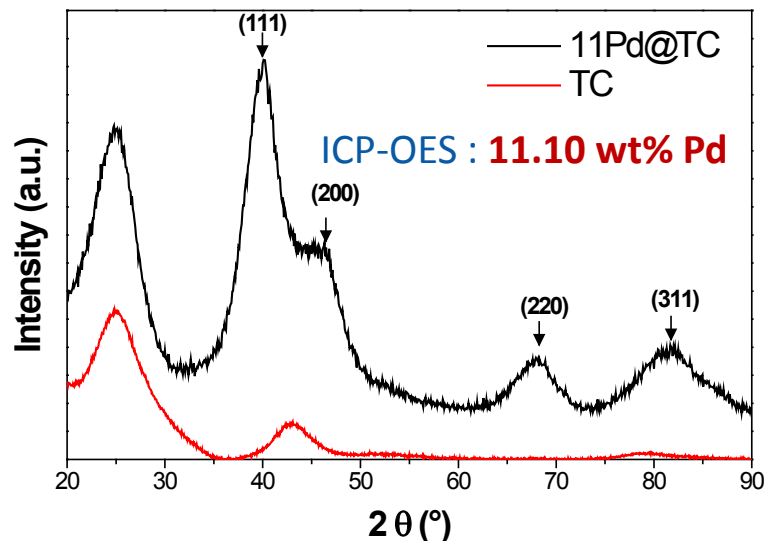
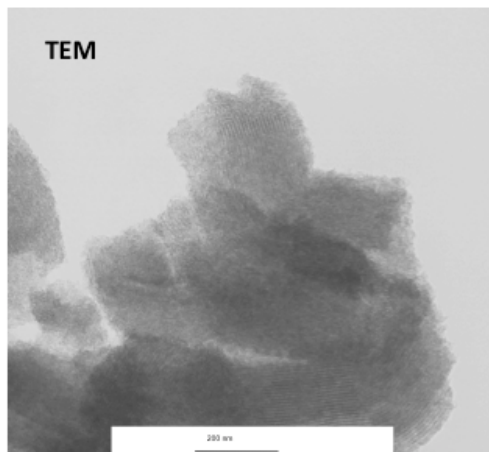
Materials systems: (Milestone 2, 67% completed, samples synthesized, measurements pending)

- Pt/Templated Carbon
- Ru/BC_x
- Pd/Templated Carbon

Workshop participants: NREL, Air Products, Univ of Toledo, Penn State, NIST, Institut de Chimie et des Materiaux de Paris Est, Max Planck-Institut für Metallforschung-Stuttgart, Rice University, Univ of Hawaii, LANL, DOE Tech Team.

Technical Accomplishments and Progress: Materials Synthesis and Characterization, Pd-Templated Carbon

March 2011: Synthesis and characterization of Templated Carbon (TC) and Pd@TC

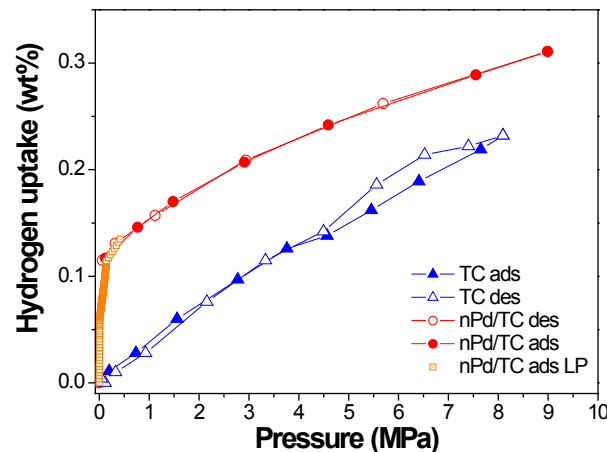


Structural properties: Pd nanoparticles adopt fcc structure

$SSA_{BET} = 810 \text{ m}^2\text{g}^{-1}$,

298 K

- nPd/TC absorbs hydrogen < 0.1 Mpa
 - Accepted H/Pd = 0.3-0.4 for nPd
 - Observed 0.6 H/Pd-TC
- Weak chemisorption observed?

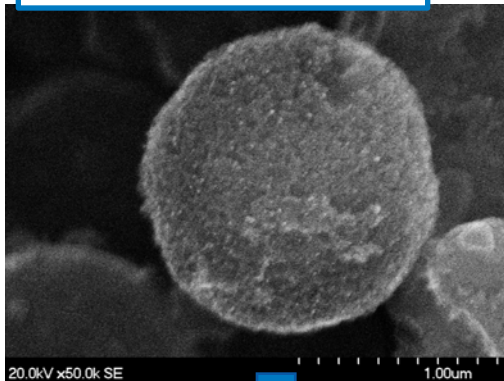


Materials for round-robin are pending volumetric and DRIFTS analysis.

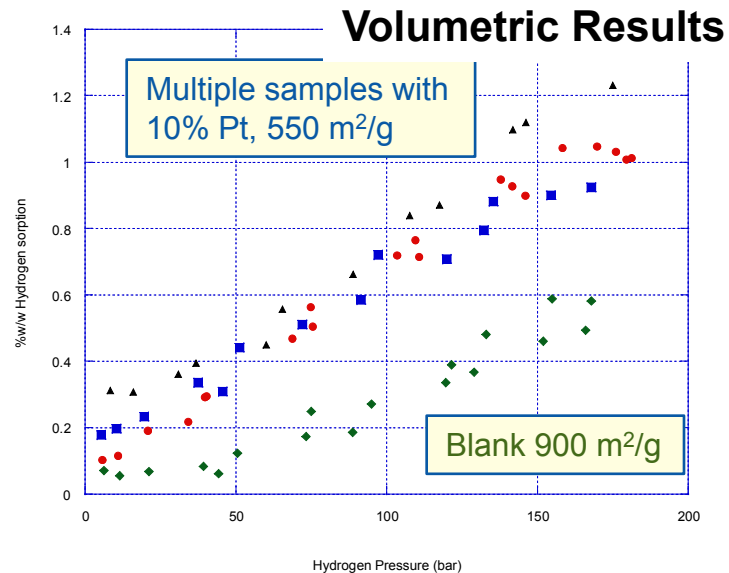
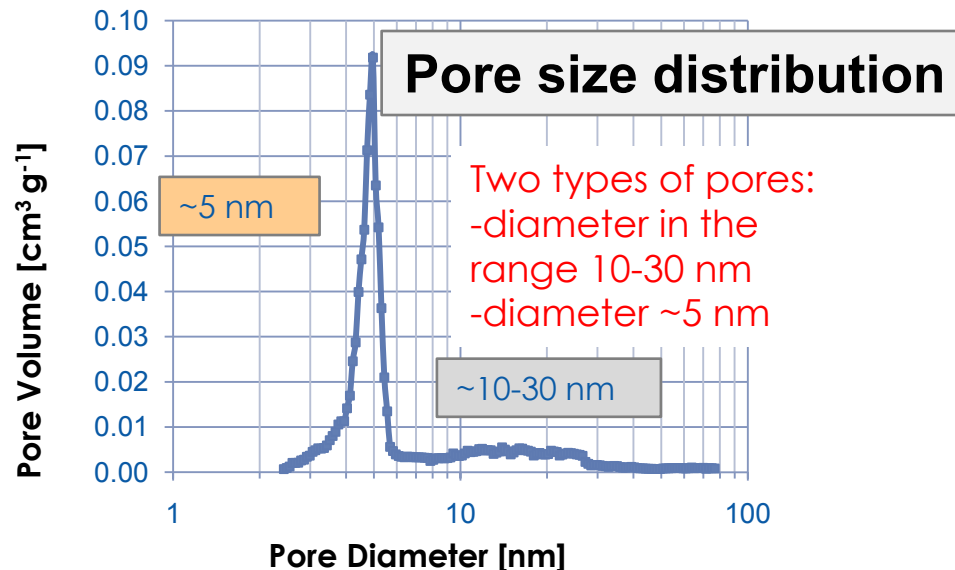
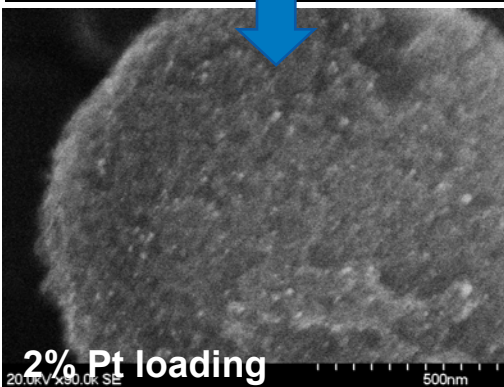
Technical Accomplishments and Progress: Materials Synthesis and Characterization: Pt-silica templated carbon

12/2010 – April 2011: Silica Templated Carbon Materials.

~ 950 m²/g
(for 5-20 nm pores)



**Microemulsion &
Micelle
Templating
Bimodal Pore Size
Distribution**

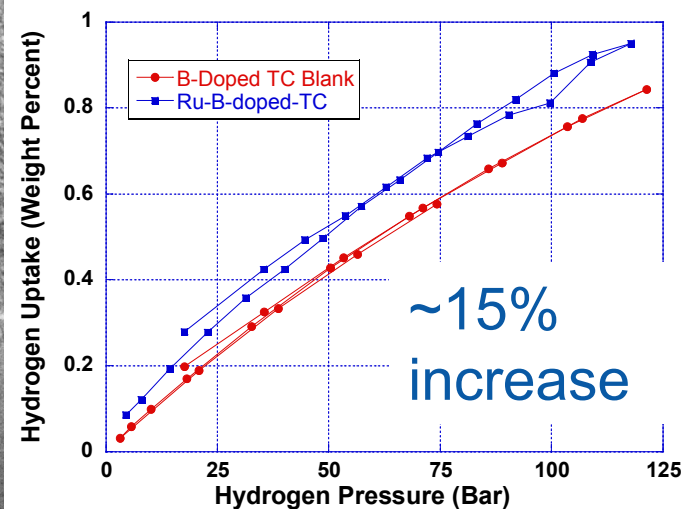
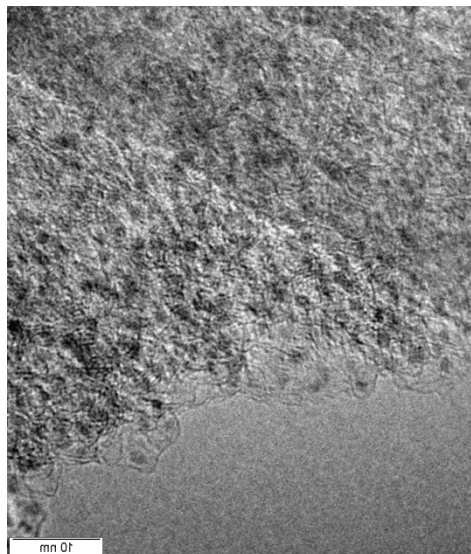


**Materials for round-robin are pending
volumetric and DRIFTS analysis.**

Technical Accomplishments and Progress:

Materials Synthesis and Characterization: Ru-BC_x materials

- Synthesized B-substituted carbon coated CMTEc, $\sim 1200 \text{ m}^2/\text{g}$.
- 2 nm dia., 8 wt% Ruthenium deposited.
- Improved kinetics
 - 25x faster than similar carbon materials.
 - 95% of adsorption occurred in 10 minutes.



Boron substitutional materials via template (BC_x), substantially improves weak chemisorption kinetics and sorption capacity

- Rates substantially faster (10 minutes vs 4 hrs)
- Minimal irreversible component
- Stable in air

Materials for round-robin are pending volumetric and DRIFTS analysis.

Approach: Status and Accomplishments

- **November 2010:** Complete standard sample(s) exchange and measurement validation.
- **November 2010:** Subcontracts paperwork initiated.
- **December 2010:** Synthesize selected spillover validation materials, Initiate Drifts Protocol
- **April 2011 (Adjusted from subcontract delays):** Exchange initial set of spillover samples
- **April 2011:** Perform additional characterization on samples
 - Samples to NREL, Hawaii, and NIST for NMR, DRIFTS, Neutron measurements, respectively.
- **May 2011:**
 - Present initial results at DOE AMR.
 - Weak Chemisorption Collaboration Group meeting
 - Samples sent to SwRI and LANL to provide additional sorption capacity confirmation.
- **June 2011: Individual Laboratory** synthesis of selected weak chemisorption material(s)
 - Establish type of C-H interaction from targeted materials
 - Complete evaluation of weak chemisorption process exchange-present results at Gordon Conference (July 2011).
- **August 2011:** Present results at Hydrogen Symposium at the ACS meeting in Denver, CO.
- **September 2011:** Present to IEA-HIA Task 22 Hydrogen Storage Research and Development meeting, Copenhagen, Denmark.

Approach – FY10-11 Milestones

2011	1	Complete standard sample(s) exchange and measurement validation	11/2010	90% complete
	2	Exchange initial set of spillover samples. Coordinate focus group efforts at IEA-HIA Task 22 Meeting (Australia) (subcontract/NDA delays of milestone)	01/2011	67% complete
	3	Complete Weak Chemisorption Focus Group meeting and report initial recommendations (at DOE Annual Merit Review)	05/2011	
	4	Establish type of C-H interaction from targeted materials.	06/2011	10% complete
	5	Complete evaluation of weak chemisorption process from exchanged materials.	07/2011	
	6	Complete meeting open to general public who may be interested, to report results on exchanged weak chemisorption samples. Will be held at ACS meeting in Denver.	08/2011	20% complete

Technical Accomplishments and Progress:

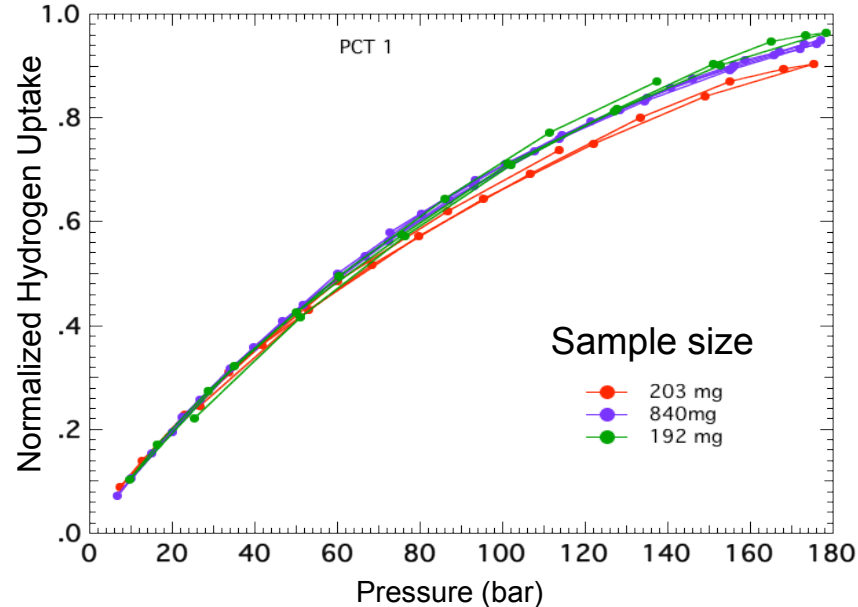
Volumetric Measurement (Milestone 1)

Coordination of efforts for inter-laboratory comparison of results to minimize measurement scatter across laboratories.

- **Null calibration**: Critical calibration. Instrument ability to measure zero adsorption/desorption.
 - Inadequate calibration causes a large systematic error.
 - Non-constant/irreproducible temperature profile of instrument.
 - Inadequate data analysis model.
 - Improper calibration procedure.
- **Absolute calibration**: Instrument ability to measure the correct magnitude for adsorption/desorption.
- **Sample mass**: large enough to ensure the true signal dominates over random and systematic errors.

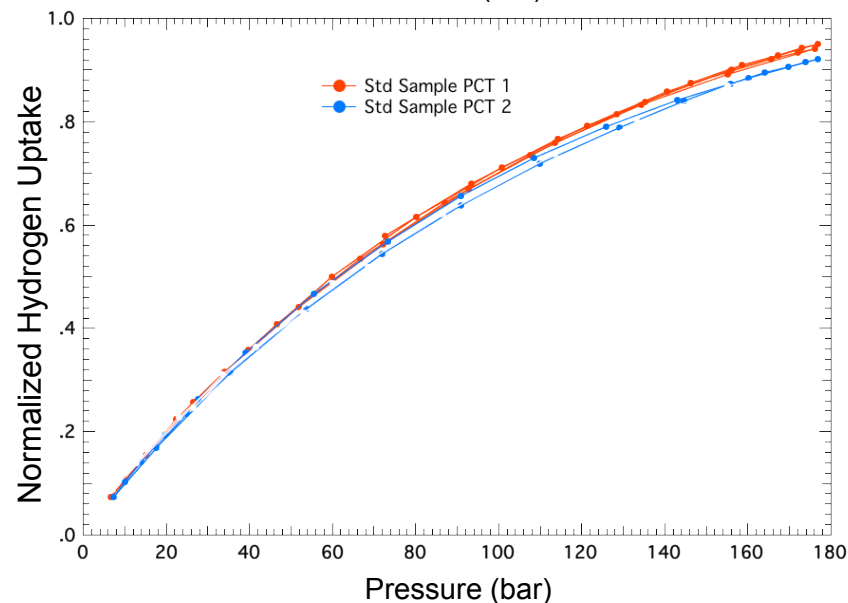
Best Practices link: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html

Technical Accomplishments and Progress: (FY 11 Milestone) Volumetric Measurement Validation



Representative data of multiple samples.

- Error bars are +/- 5%.
 - Sample size 150 mg – 1 gram.
- Improved with corrections for temperature fluctuations between measurements.



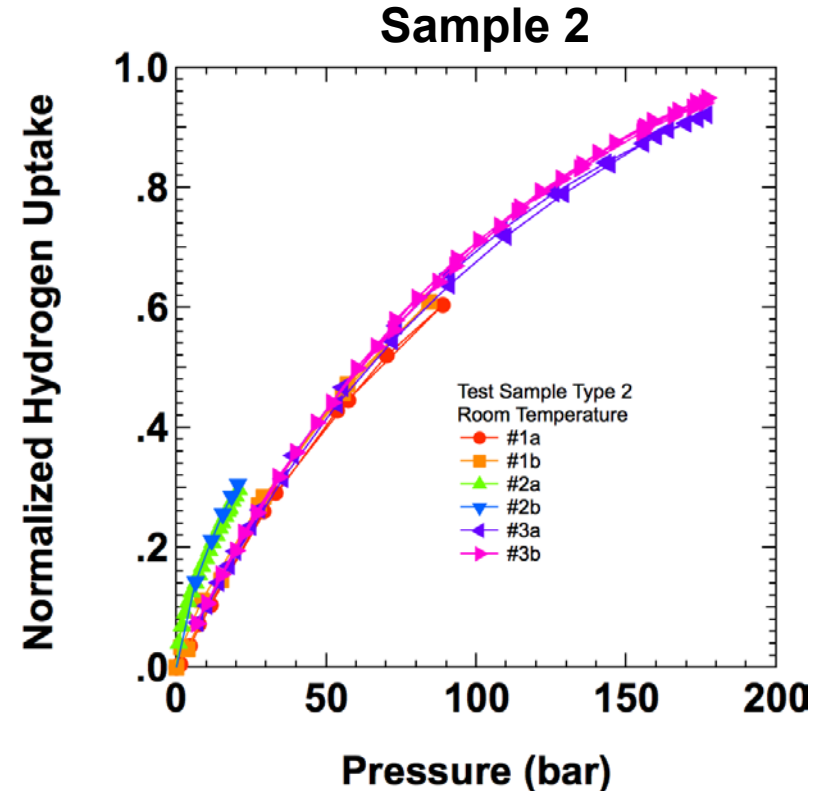
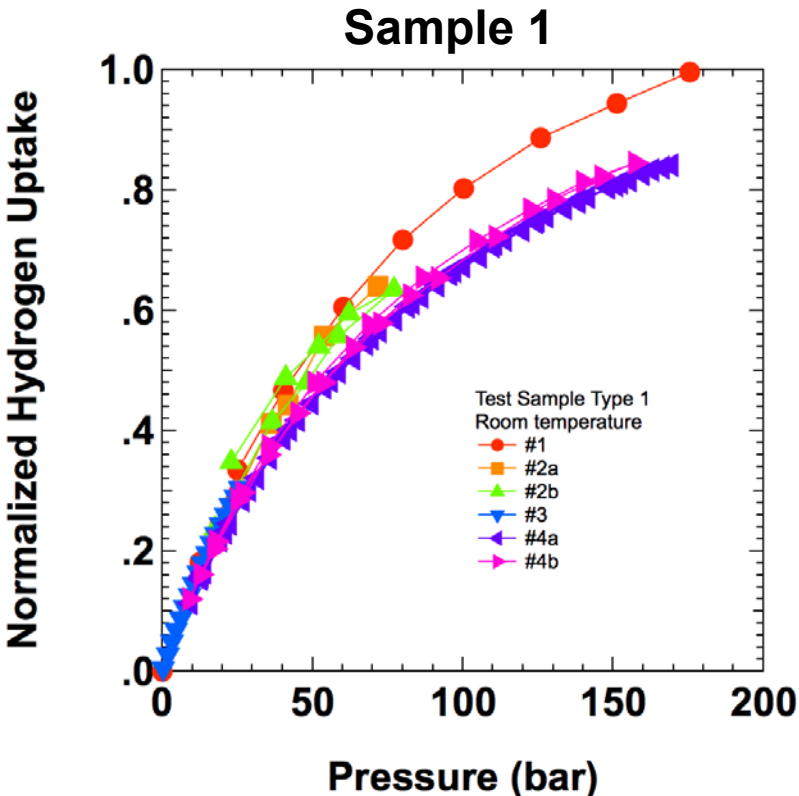
2 instruments
2 scientists
Same sample (≈ 500 mg)

Reproducible with error < 2 % for two different instruments.

NREL established accuracy and precision limits of our volumetric instrumentation.

Technical Accomplishments and Progress: Inter-Laboratory Comparison of Volumetric Data, FY 11 Milestone

Data normalized until the inter-laboratory comparison is complete.



Variations in Results

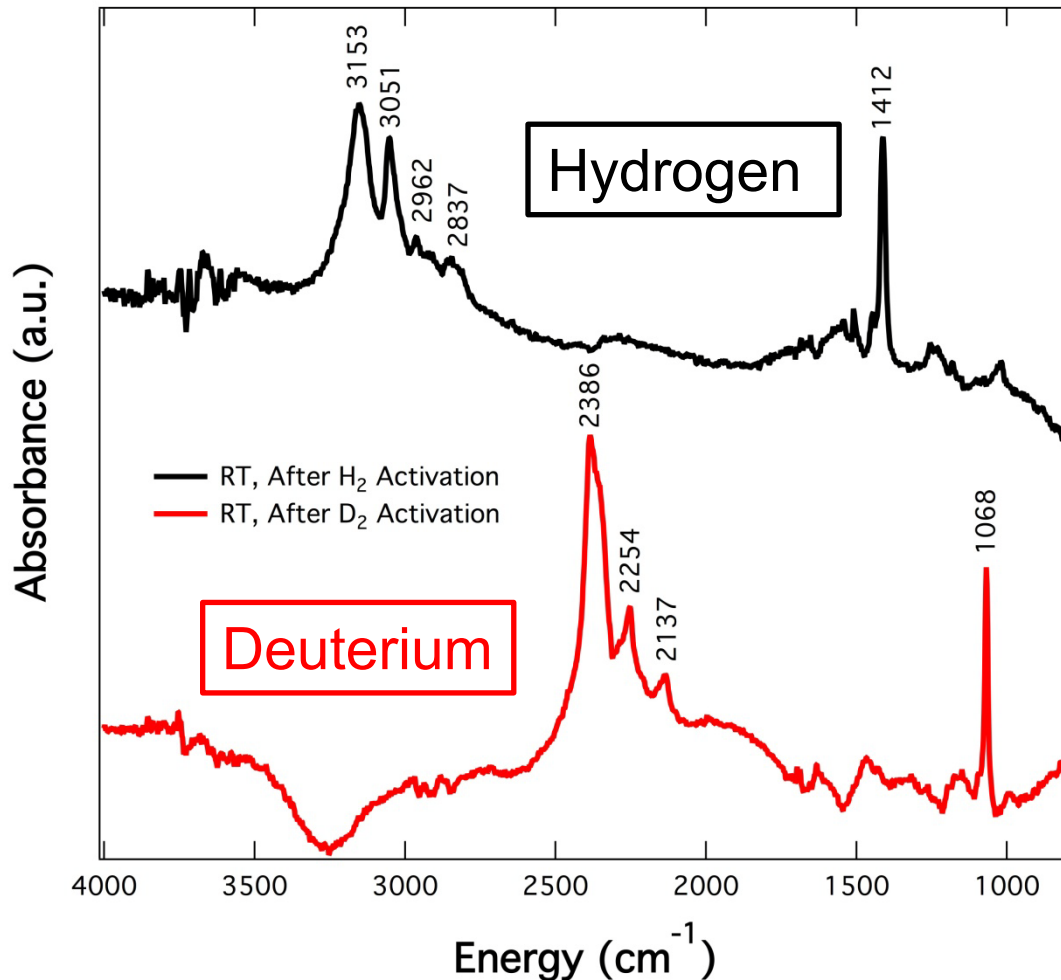
- **Working with partners/collaborators to establish cause of variability.**
 - Correction factor variations
 - Temperature fluctuations
 - Second set of experiments underway

Technical Accomplishments and Progress: Portfolio of Measurements

- DRIFTS (NREL) Diffuse Reflectance Infrared Fourier Transform Spectroscopy
 - Establish surface chemistry of high surface area powders
 - Under high pressure, establish the type of interaction for spillover hydrogen/deuterium.
 - C-H or C-D
 - O-H or O-D
- NMR (University of Hawaii)
 - Quantify the relative populations of physisorbed and spillover hydrogen.
 - High pressure T1 relaxation studies and spectral deconvolution of overlapping signals for physisorbed, “spillover”, and free gaseous hydrogen.
 - Elucidation of the chemical environment of the spillover hydrogen.
 - Cross-polarization experiments on ^{13}C , ^{15}N , and ^2H labeled samples
- Neutron Scattering (NIST)
 - Provide critical information on sorbent capacity, bonding states, dynamics and structure aspects for spillover materials.

Technical Accomplishments: DRIFTS Investigation of “Spillover” Hydrogen.

Comparison of H₂ and D₂ DRIFTS for Pt ETEK Carbons



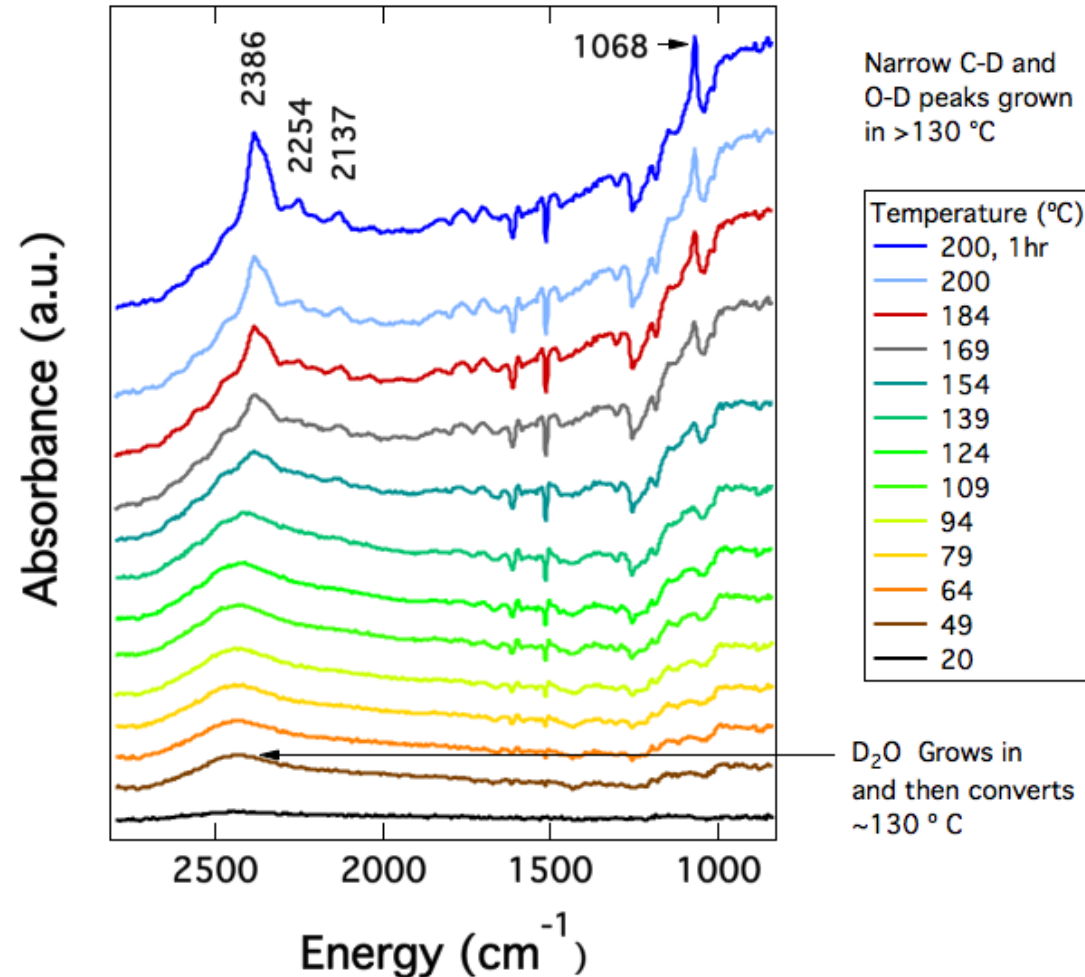
Pt ETEK Carbon:

- 40% Pt on Vulcan XC-72 activated carbon
- Activations were performed at 200 °C under ~200 psi of H₂ or D₂ (Two fresh samples used)
- Spectra shown were collected at RT after the H₂/D₂ activations
 - 3153 cm⁻¹: Surface O-H
 - 3051 to 2837 cm⁻¹: Surface C-H
 - 2386 cm⁻¹: Surface O-D
 - 2254 to 2137 cm⁻¹: Surface C-D
- The appearance of peaks at 1412 and 1068 after H₂ and D₂ activations, respectively.

New spectral lines at 1412 and 1068 cm⁻¹ preliminarily assigned to new C-H/C-D deformation.

Technical Accomplishments: DRIFTS Investigation of “Spillover” Hydrogen.

DRIFTS results illustrate the formation of a covalent C-D Bonds



Pt E-TEK Carbon:

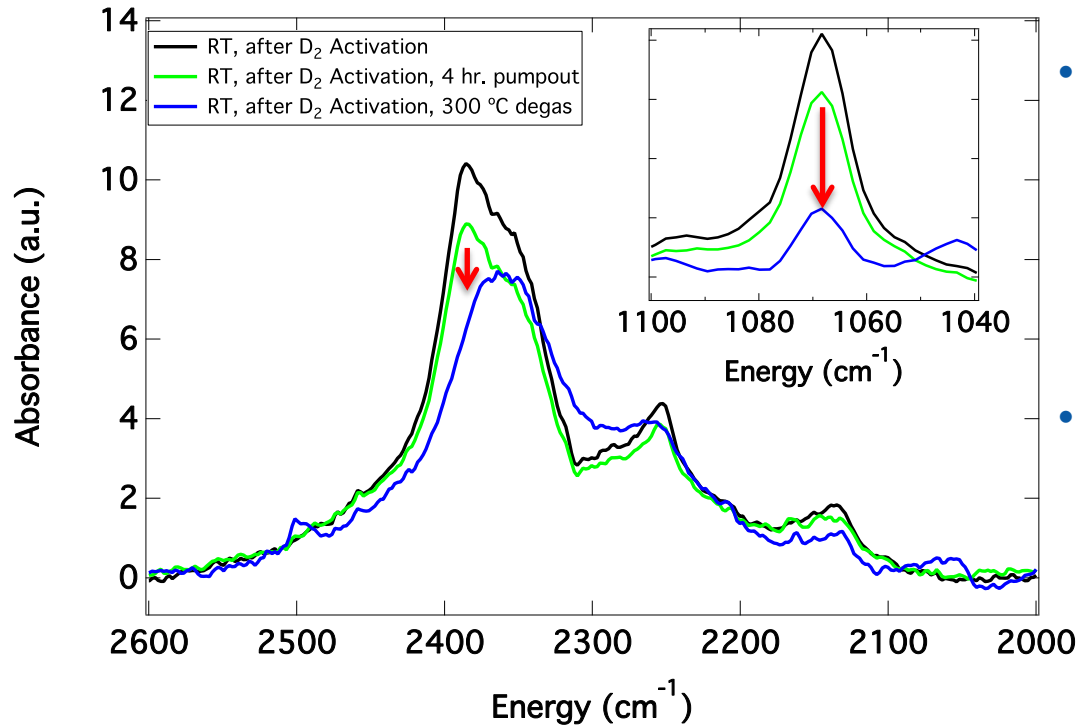
- 40% Pt on Vulcan XC-72 carbon
 - Establish approximate IR peak positions.
 - XC-72 efficient hydrogen dissociation reaction at fuel cell anode.
- 50-100 mg sample size required as compared to 5 grams for neutron scattering experiments.

Deuterium Activation:

- Slowly heat sample to 200°C under 10 bar D_2 .
 - Heat accelerates kinetics of spillover reaction
- Surface-bound D_2O initially formed (2441 cm^{-1})
- After $\sim 130^\circ\text{C}$, new sharp peaks form
 - 2386 cm^{-1} : Surface O-D
 - $2137, 2254\text{ cm}^{-1}$: Surface C-D
 - **1068 cm^{-1} : C-D deformation**

Technical Accomplishments: DRIFTS Investigation of “Spillover” Hydrogen.

Stability of Surface Species formed by D₂ Activation



- Stability of the newly formed surface species was monitored by DRIFTS during a RT and 300 °C degas. (Heat used to enhance kinetics of desorption.)
- Peak area remaining after 300 °C degas:
 - 2100 to 2600 cm⁻¹: 70%
 - 1050 to 1090 cm⁻¹: 20%

The sharp peak at 2386 cm⁻¹ disappears in concert with the 1068 cm⁻¹ peak, suggesting that the 1068 cm⁻¹ peak may possibly be due to weak C-D bonds. (Pt – D signal is >1400 cm⁻¹)

Collaborations & Project Participants

NREL: Coordinate validation of standard samples, synthesis of B-Doped and Pt-Templated Carbon samples, Develop DRIFTS for high pressure hydrogen sorption analysis, volumetric analysis. Evaluate/coordinate volumetric protocols.

Institut de Chimie et des Materiaux de Paris Est, Michel Latroche: Pd-templated carbon synthesis and isotopic labeling

Max Planck-Institut für Metallforschung-Stuttgart, Michael Hirscher: Volumetric analysis, Isotopic Labeling experiments, synthesis of standard samples

University of New Mexico: Plamen Atanassov: Porous Silica Templated Carbon with Pt Synthesis, XPS analysis

University of Hawaii, Craig Jensen for volumetric measurements and high pressure NMR.

Other Project Participants:

NIST, Craig Brown: Neutron scattering, Volumetric Analysis measurements.

Penn State University, Angela Lueking: Sample synthesis and Volumetric/Gravimetric analyses.

LANL, Tony Burrell: Volumetric analysis and synthesis.

Univ Michigan, Ralph Yang: Sample synthesis.

Curtin University, Craig Buckley: Volumetric analysis.

Kyushu University, Etsuo Akiba: Volumetric analysis and synthesis .

Griffith University, Evan Gray: Volumetric Analysis to 700 bar.

Proposed Future Work

- **Complete round-robin of standard samples (completed)**
 - Working with partners from around the world to achieve virtually identical hydrogen capacity measurements on the same sorbents
- **Complete synthesis of the different spillover samples and distribute initial set to the different labs for evaluation. (completed)**
- **Down select validated spillover materials and distribute samples to other labs for validation and additional characterization. (May 2011)**
- **Synthesis of validated spillover materials by other labs. (June 2011)**
- **Demonstrate spectroscopic evidence for spiltover C-H bonds. (June 2011)**
 - DRIFTS, NMR, Neutron Scattering
- **Report detailing findings and recommendations. (Gordon Conference, July 2011)**
- **Report final findings: ACS conference, (August 2011) and IEA-HIA Task 22 Hydrogen Storage Meeting. (September 2011)**

Summary

- Organized and held workshop with expert panel.
 - Major recommendations:
 - reproducible synthesis
 - measurement validation
 - spectroscopic evaluation of hydrogen-substrate interaction
- Three materials downselected for analysis.
 - high probability of demonstrating reversible weak chemisorption of hydrogen
 - synthesized and validated in different laboratories.
- Sample exchanges and measurements being performed.
 - Standard sample validation of volumetric measurements.
 - Synthesis of materials downselected for analysis
- Identified DRIFTS, NMR and Neutron measurements as most appropriate for observing C-H bonding.
- Preliminary DRIFTS illustrate stretching regions expected for the spillover C-H and C-D bonds. NMR experiments initiated April 2011. Neutron analysis pending.

Validation and recommendations of weak chemisorption processes by this effort will enable the hydrogen sorption community to accelerate development of room temperature hydrogen storage materials for light duty vehicle and other early market applications.

Technical Back-Up Slides

Approach

Validation Effort of Room Temperature Hydrogen Chemisorption, i.e. Spillover.

International Collaborative Effort

- Michael Hirscher, Max Planck, Germany
- Michelle Latroche, ICMPE, France
- Angela Lueking, Penn St, USA
- Craig Jensen, Univ of Hawaii, USA
- Craig Brown, NIST, USA
- Tony Burell, LANL, USA
- Plamen Atanassov, Univ New Mexico, USA
- Thomas Gennett, NREL, USA

Specific Objectives Established:

- Well defined synthesis and activation of materials demonstrated across participant laboratories
- Universal reproducibility of enhanced adsorption effects (>15% enhancement for samples across laboratories) with reproducible uptake and release of hydrogen in desired temperature range (5-10 cycles).
- Spectroscopic identification of binding sites and state of hydrogen (atomic, molecular, other) and transport with advanced *in-situ* techniques.
 - IR (DRIFTS)
 - NMR
 - XRD/XPS
 - Neutron Scattering
 - Isotopic labeling experiments
- Utilize characterization information to update, integrate, and validate current mechanistic models.

Conduct experiments with narrow range of materials that exhibited an apparent hydrogen spillover process at < 40 °C

- Establish a baseline protocol for all volumetric measurements to confirm accuracy and sensitivity.
 - Max Planck-Stuttgart, NREL, LANL, NIST, SWRI, Penn St., ICMPE, etc)

Characterization with spectroscopic tools.

- IR, NMR and Neutron measurements under elevated hydrogen pressures (1 - 200 bar)
- Determine the nature of interactions (C-H, O-H, Hydrogen bonding, etc)

Key issues:

- Establish uniform measurement protocols
- Lack of reproducibility in measurements and synthesis.
- Slow kinetics of hydrogen adsorption
- Low concentration of “spillover” hydrogen wrt detection limits of instrumentation
- Reconcile spillover to thermodynamic limits.
 - Predictive versus observed hydrogen-catalyst-substrate interactions
 - Translate observed physisorption and/or chemisorption interactions to thermodynamic and kinetic barriers

Characterization by NMR

High Pressure (up to 1.5 kbar), Low Temperature Wide-line ^1H NMR Studies.

- T_1 studies and spectral deconvolution of overlapping signals for physisorbed, “spillover”, and free gaseous hydrogen. Differentiation through comparison of spectra of hydrogen physisorbed on carbon substrates to those of materials verified to contain both “spillover” and physisorbed hydrogen.
- Quantify the relative populations of physisorbed and spillover hydrogen.

Cross-polarization Experiments on ^{13}C , ^{15}N , and ^2H Labeled Samples

- Elucidation of the chemical environment of the “spillover” hydrogen.
- Determine if C-H, N-H, or H-H (D-H), and/or O-H bonding is present within spillover materials.

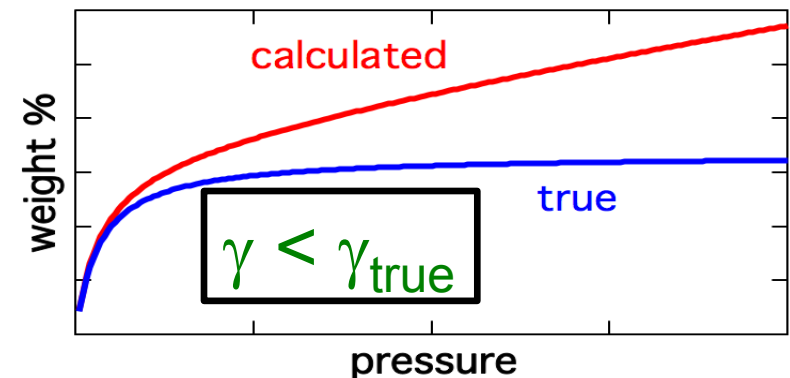
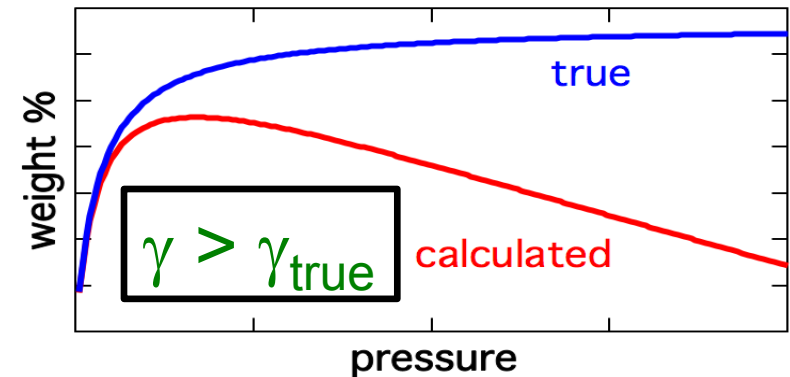
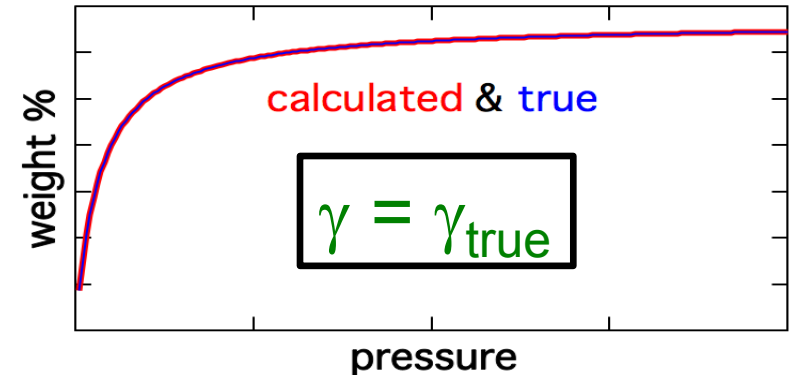


University of Hawaii

Technical Accomplishments: What Systematic Error Look Like.

- Null calibration constant is called γ and it can have an error associated with it:
 - $\gamma = \gamma_{true} + \gamma_{err}$
- γ error can be positive or negative so systematic error in moles can add or subtract from the true adsorption signal
- It is a roughly linear signal with pressure:

$$N_{err} = \gamma_{err} \left(\frac{V_r}{RT} \right) \left(\frac{P}{z(P, T)} \right)$$



Technical Accomplishments: Precision of Calibration Necessary.

- Need:

(moles adsorbed by sample) \gg (“moles” from systematic error)

$$m_s n_{ads} \gg \gamma_{err} \left(\frac{V_{ref}}{RT} \right) \left(\frac{P_{Max}}{z(P_{Max}, T)} \right)$$

- If γ_{err} is the null calibration error and for a 200 mg sample (m_s) with 0.5 wt% H₂ at 300 K, 100 bar and $V_{ref} = 5$ ml,

$$\sim 0.025 \gg \gamma_{err}$$

- So γ_{err} should be ~ 0.0025 for 10% error and ~ 0.00025 for 1% error; since $\gamma \sim 2$ for most instruments, 0.1% to 0.01% relative error is needed for γ calibration

- **→ very careful calibration required!**

Technical Accomplishments and Progress: Best Practices for Characterizing Engineering Properties of *Hydrogen Storage Materials*

PI: Karl Gross, H2 Technology Consulting LLC

- **Document:** 515 pgs, 7 sections: Introduction, Capacity, Kinetics, Thermodynamics, Cycle-Life, Thermal Properties, Mechanical Properties measurements.
- **International Collaboration:** 14 co-authors, 22 expert reviewers, 10 countries

Accomplishments: 2010/2011

- **Finalize Updated Capacity Section 100%:** Public input on Spill-over effects were addressed, reviewed by NREL and incorporated into document.
- **Finalize Thermodynamic section 95%:** Final review of the Thermodynamic section has been completed and reviewer's edits and comments are currently being addressed..
- **Draft Cycle-Life Section 100%:** Draft version of the Cycle-life section completed.
- **Review of Cycle-Life Section 95%:** Initial review and integration of edits and comments completed, delivered to NREL, final review near completion.
- **Draft Thermal Properties Section 15%:** Draft version in progress with 2 expert coauthors.

Current version Best Practices document available at:

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html