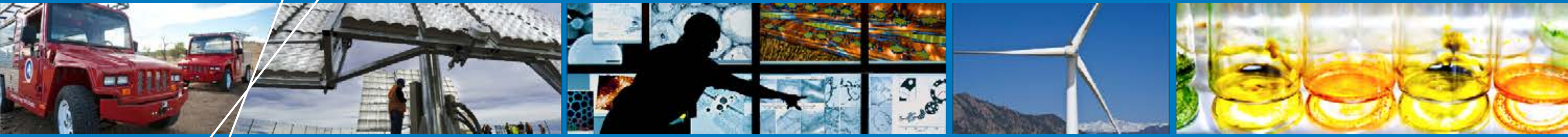
Hydrogen Sorbent Measurement Qualification and Characterization



Philip Parilla
National Renewable Energy Laboratory
June 8, 2016

st014

Overview

Timeline*

Start: October 2015

End: to be determined

% complete FY 16: ~65%

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

Budget

Funding FY15: $575K

Funding FY16: $1.206M

Total Multi Performer Project Funding: $2.806M#

#Includes LBNL, PNNL, and NIST

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

NIST – Craig Brown, Terry Udovic

PNNL – Tom Autrey, Mark Bowden

LBNL – Jeff Long, Martin Head-Gordon

HyMARC

LANL, USA – Troy Semelsberger

H2Technology Consulting, USA – Karl Gross

H_2ST^2, USA – Hydrogen Storage Tech Team

IEA-HIA Task 32 – Michael Hirscher, Darren Broom

Outline: Three Research Activity Areas

- **Volumetric Capacity Protocols**
  - Develop recommended measurement and analysis protocols
  - Disseminate results to storage community
- **Thermal Conductivity Measurements for H_2 Storage Materials**
  - Develop measurement hardware & procedures
  - Measure at variable temperatures and gas pressures
  - Validate measurements using known materials
- **Verification and Error Analysis for H_2 Capacity Measurements**
  - Independently measure capacities to verify claims
  - Conduct inter-laboratory comparison for volumetric capacity measurements

Relevance: Volumetric Capacity Protocols

DOE Objective:

Volumetric capacity metrics are critical for technological and commercial development; they must be calculated and reported in a uniform and consistent manner to allow comparisons among different materials. There needs to be a uniform protocol for determining and reporting on volumetric capacity.

Project Goals:

Develop Volumetric Capacity Protocols

- 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.
- Develop protocols for the determination of volumetric capacity of sorbent materials.
- Submit a report that will be disseminated to the scientific community.

Relevance: Importance of Volumetric Capacity

- Volumetric Capacity (VC) is a crucial figure of merit (FOM) to evaluate H_2 storage materials.
- Need standardized and well-defined VC definitions and protocols to provide uniform practices.
- We have explored and clarified VC conventions and protocols resulting in guidelines for VC implementations.
- We solicited external participation (IEA and H_2ST^2) to ensure a careful & comprehensive implementation.

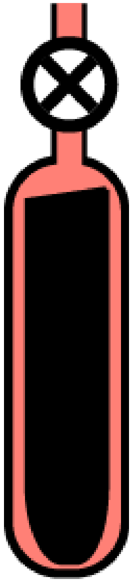
Approach: Addressing the Issues

- **Conventions**
  - Accounting for hydrogen
    (Accurate counting! No double counting.)
  - Accounting for volumes
  - Best FOM for a given situation

$$\Lambda_{VC} = \sum_i m_{i\,H_2} \Big/ \sum_i V_i$$

g H_2/L

- **Measurement Protocols**
  - Implementing the conventions into practice
  - Ancillary protocols (e.g., bulk & skeletal densities)
- **Sample Preparation**
  - Standard preparation (degassing, activating)
  - Sample compaction/densification



Accomplishments: Best FOM for a Given Situation

- **Tailor volumetric capacity FOM to target specific goals**
  - Material evaluation, comparison and optimization
  - Engineering considerations and system optimization
- **Seven FOMs were identified as being useful *and* well-defined**
  - Which one to use depends on material type and goals; can be used for both adsorption and absorption materials.
  - Each FOM can be calculated easily from the same isotherm data sets so it is feasible to report on all seven.
  - **FOMs based on absolute capacity are NOT recommended as the absolute adsorption volume is not well-defined.**
- **Volumetric Capacity Protocols Published!**
  - *"Recommended Volumetric Capacity Definitions and Protocols for Accurate, Standardized and Unambiguous Metrics for Hydrogen Storage Materials"*, P. A. Parilla, K. Gross, K. Hurst, T. Gennett " *Appl. Phys. A*. 122; 201, 2016
  - Developed short written guidelines for reporting results in papers and presentations.

Accomplishments: Seven Volumetric Capacity FOMs

Recommended Volumetric Capacity FOMs

Symbol	Description
Λ_{ec}	Volumetric capacity FOM based on *excess* capacity/crystal volume
Λ_{ep}	Volumetric capacity FOM based on *excess* capacity/packing volume
Λ_{nm}	Volumetric capacity FOM based on *net* capacity/empty vessel volume
Λ_{np}	Volumetric capacity FOM based on *net* capacity/ packing volume
Λ_{tc}	Volumetric capacity FOM based on *total* crystal capacity/crystal volume
Λ_{tp}	Volumetric capacity FOM based on *total* capacity/packing volume
Λ_{ts}	Volumetric capacity FOM based on *total* capacity/total system volume

Definitions, measurement protocols, analysis procedures and reporting recommendations are given in the *Applied Physics A* publication.

Accomplishment: Guidelines for Communicating Results Clearly

Guidelines have been produced to report results clearly in papers and presentations. Example checklist:

Checklist For Reporting On Capacity For Hydrogen Storage Materials In Presentations

☐ For gravimetric capacity, use weight % (wt%) as defined in eq.1 using the excess capacity.

☐ For volumetric capacity, use total volumetric capacity based on packing volume (eq. 5a).

☐ If total crystalline volumetric capacity is used, make sure it is labeled as such. If possible, separately provide total volumetric capacity based on packing volume.

☐ Identify the pressures and temperatures associated with each capacity that was calculated.

☐ Report on sample form factors such as powder, pellets, disk, etc.

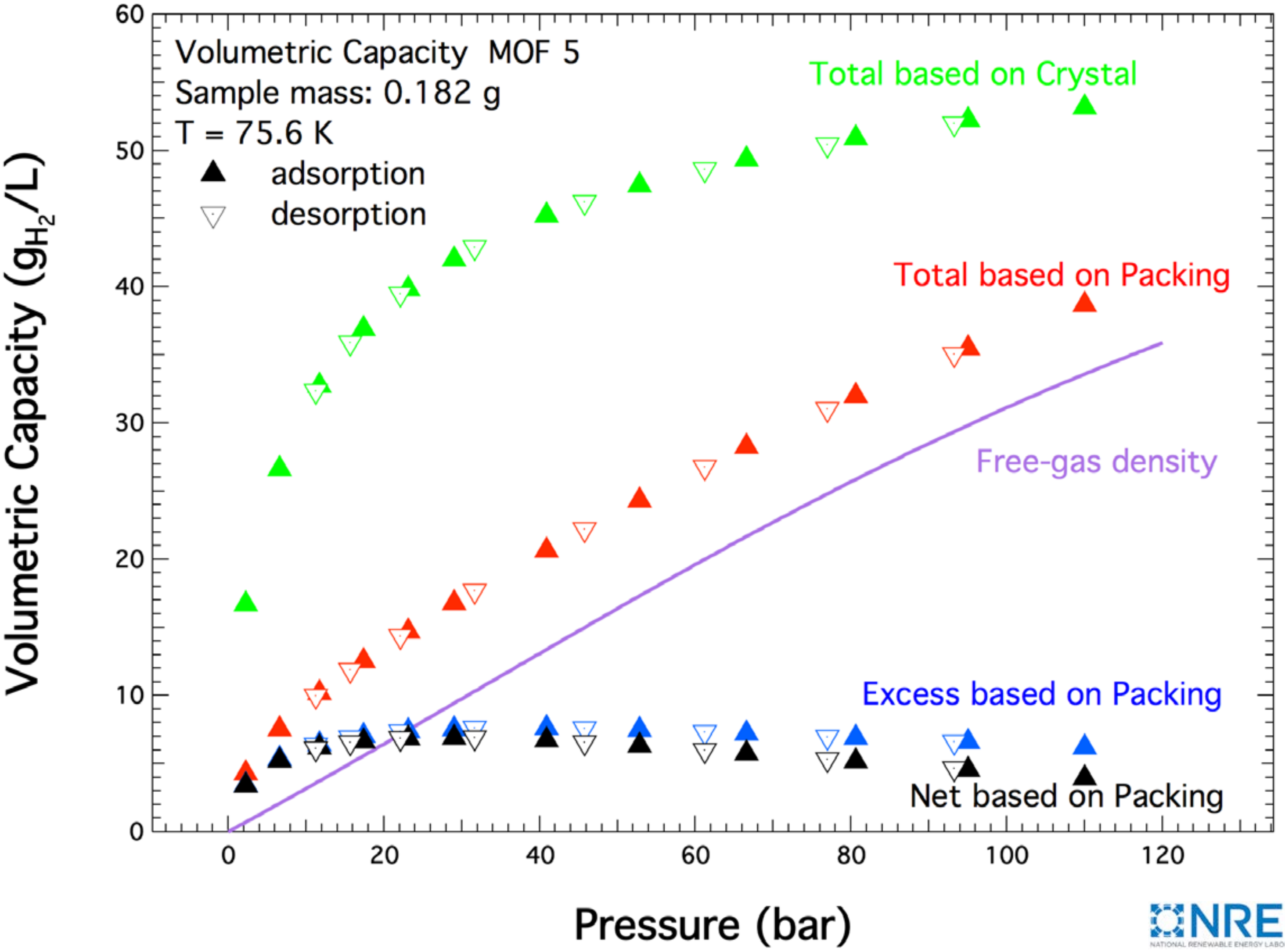
☐ Report on final sample mass used for capacity determinations.

☐ Be able to describe the following through tables, backup slides or handouts:

1) Procedures and results for determining sample skeletal volume, V_{sk} or skeletal densities.
2) Procedures and results for determining sample packing volume, V_{pk} or packing (bulk) densities.
3) Procedures and results for determining sample V_{crys} or crystalline densities.

Volumetric Results Depends on Assumptions

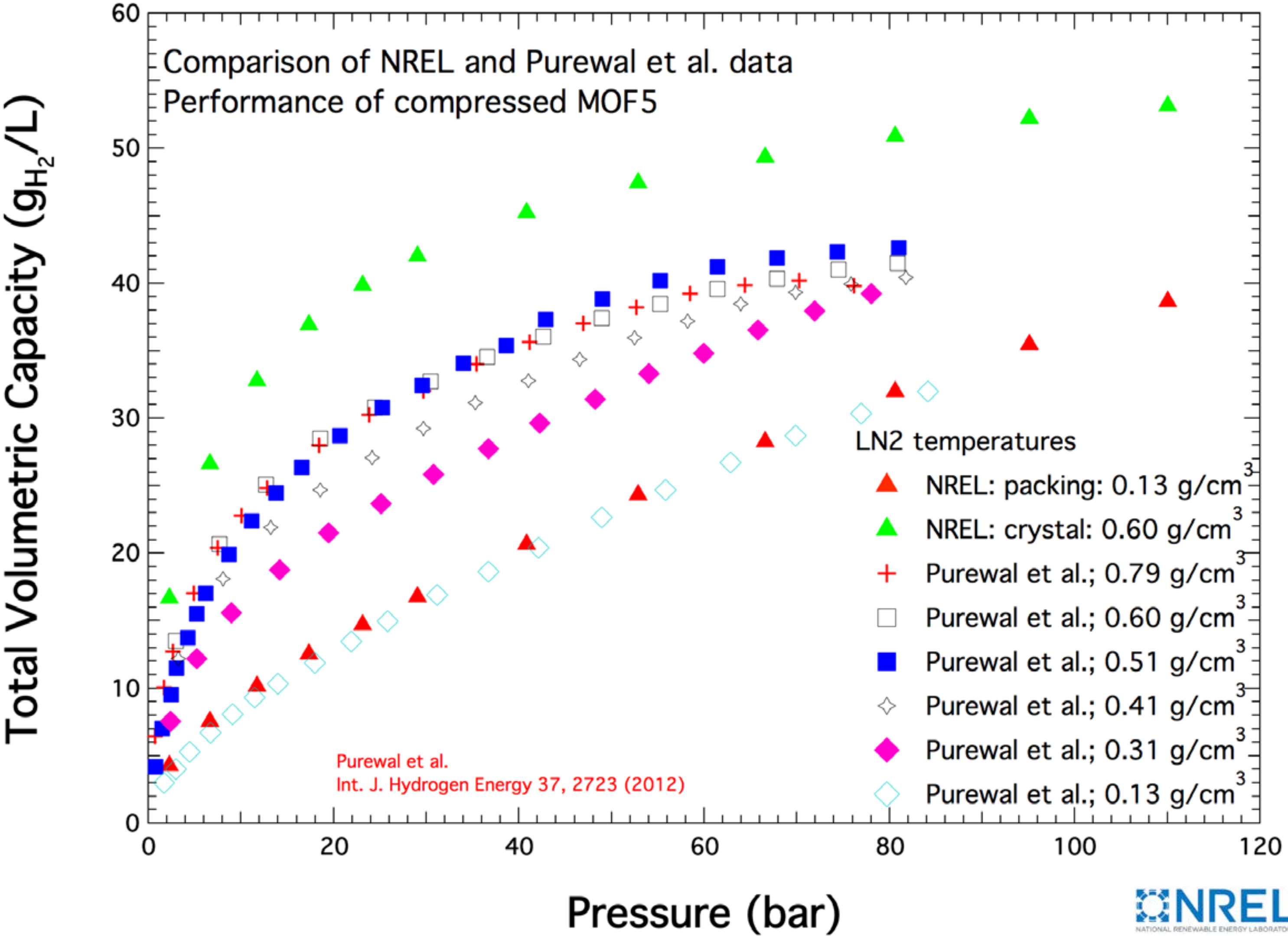
Normalization affects volumetric data



- Graph shows the same raw data calculated with different H_2 capacity determinations.
- Note the difference between the Total capacities based on crystalline and packing densities.

Sample Densification Impacts Capacity

Packing and crystalline total volumetric capacities provides boundaries



- Densification initially improves volumetric capacity, but then “max’s out” and even starts to degrade for MOF-5.
- This highlights just one possible difficulty in trying to reach crystalline densities and maintain high capacities.

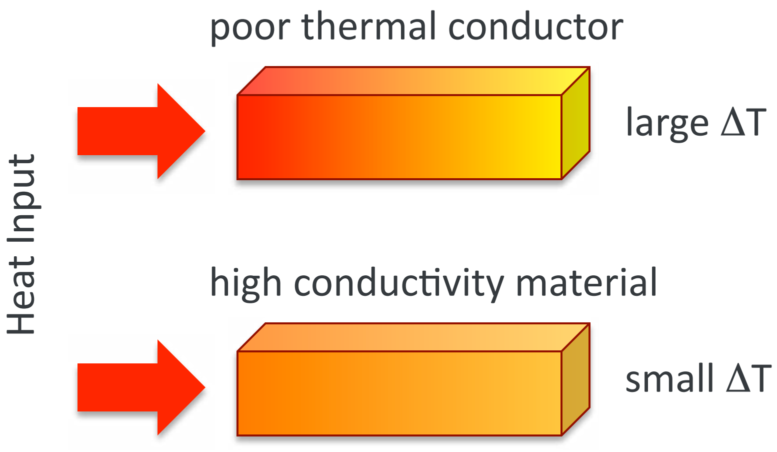
Remaining Challenges and Barriers: Volumetric Capacity

- Now that the recommendations have been published, it is critical that the hydrogen storage community put the recommendations into practice. The most direct path towards this goal is for researchers to explicitly report on the protocols and FOMs used and to label data accordingly.
- There remains a great interest and need to have a well-defined absolute capacity determination, but this is extremely difficult as the adsorption volume cannot readily be determined. There currently is no obvious solution moving forward.
- Even though excess, net, and total capacities can be determined experimentally, there is considerable interest in calculating these quantities on theoretical crystalline materials. Issues, such as double counting, have yet to be addressed in the calculations.

Relevance: Thermal Conductivity Measurement & Validation

DOE Objective:

Thermal conductivity measurements for hydrogen-storage materials must be based on valid and accurate results and be conducted under relevant operating conditions to ensure proper identification of promising materials for DOE support and provide engineering data for system design.



Project Goal:

- Develop thermal conductivity measurements for hydrogen storage materials from 77K to 400K, and at pressures up to 100 bar.
  - -Establish methodology for characterizing materials with different form factors.
  - -Validate measurement technique over entire temperature and pressure range.
- Assist materials-research groups to characterize and validate their thermal conductivity measurements.
  - -Measure external samples at NREL to supplement the source group's measurement capabilities.
  - -Validate extraordinary properties claims for novel hydrogen storage materials.

Relevance: Importance of Thermal Conductivity

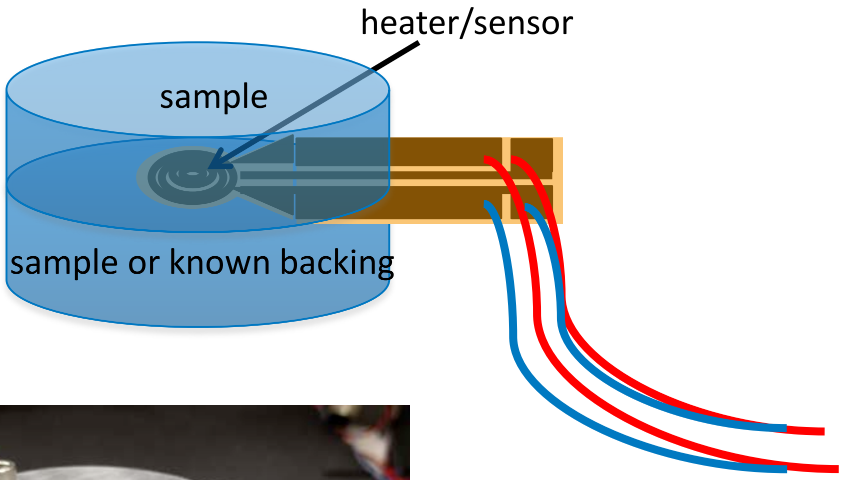
- **The thermal conductivity of the hydrogen storage material impacts the design of heat exchangers for temperature control.**
  - Low thermal conductivity materials require additives, such as graphite, and/or macroscopic heat-transfer enhancing structures such as fins in the container.
- **The thermal conductivity of the hydrogen storage materials depends on temperature and H_2 gas pressure.**
  - Accurate predictions of material performance require thermal conductivity measurements at the expected operating conditions.
- **A thermal conductivity apparatus that can measure materials over the desired temperature and pressure range is not commercially available and requires customization.**

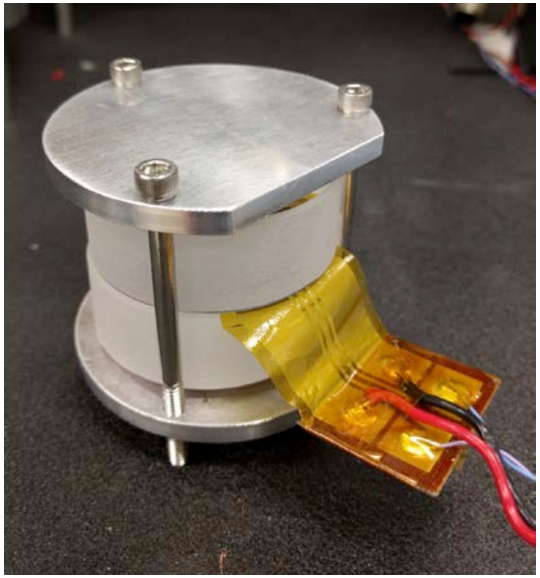
Approach: Develop a Versatile Apparatus

Design and build an apparatus capable of measuring the thermal conductivity of hydrogen storage materials under ***expected operating conditions***:

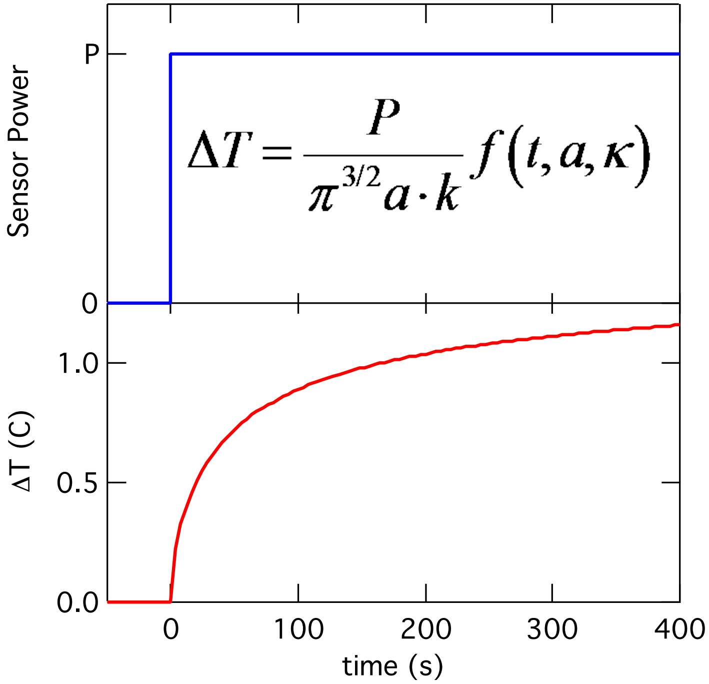
- up to 100 bar
  - modify commercial autoclave to enable thermal conductivity measurements
- 77 K to 400 K
  - modify commercial cryostat to accept autoclave
- capable of measuring pucks and powders and small-volume samples (down to ~ 0.5 cm^3)
  - design and build sample holders for different form factors (e.g. pucks, powders, small volumes)

Approach: Transient Plane Source Technique





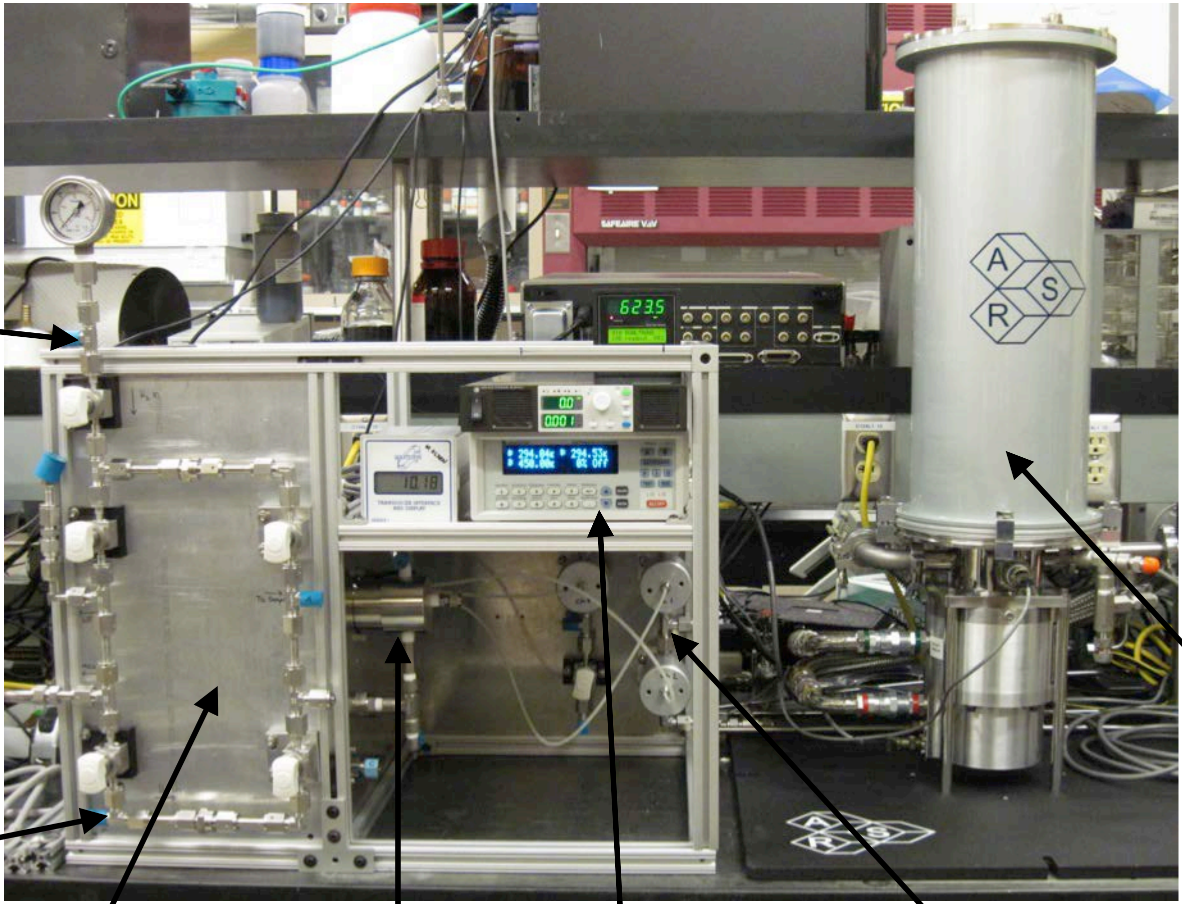
The sample holder sits inside the pressure vessel, which mounts atop a cryostat.



$$\Delta T = \frac{P}{\pi^{3/2} a \cdot k} f\left(t, a, \kappa\right)$$

Fitting the thermogram yields the thermal properties of the sample.

Accomplishments: Constructed Apparatus



Hydrogen inlet

(Control electronics behind manual valve panel)

Helium inlet

Manual valves

Pressure regulator

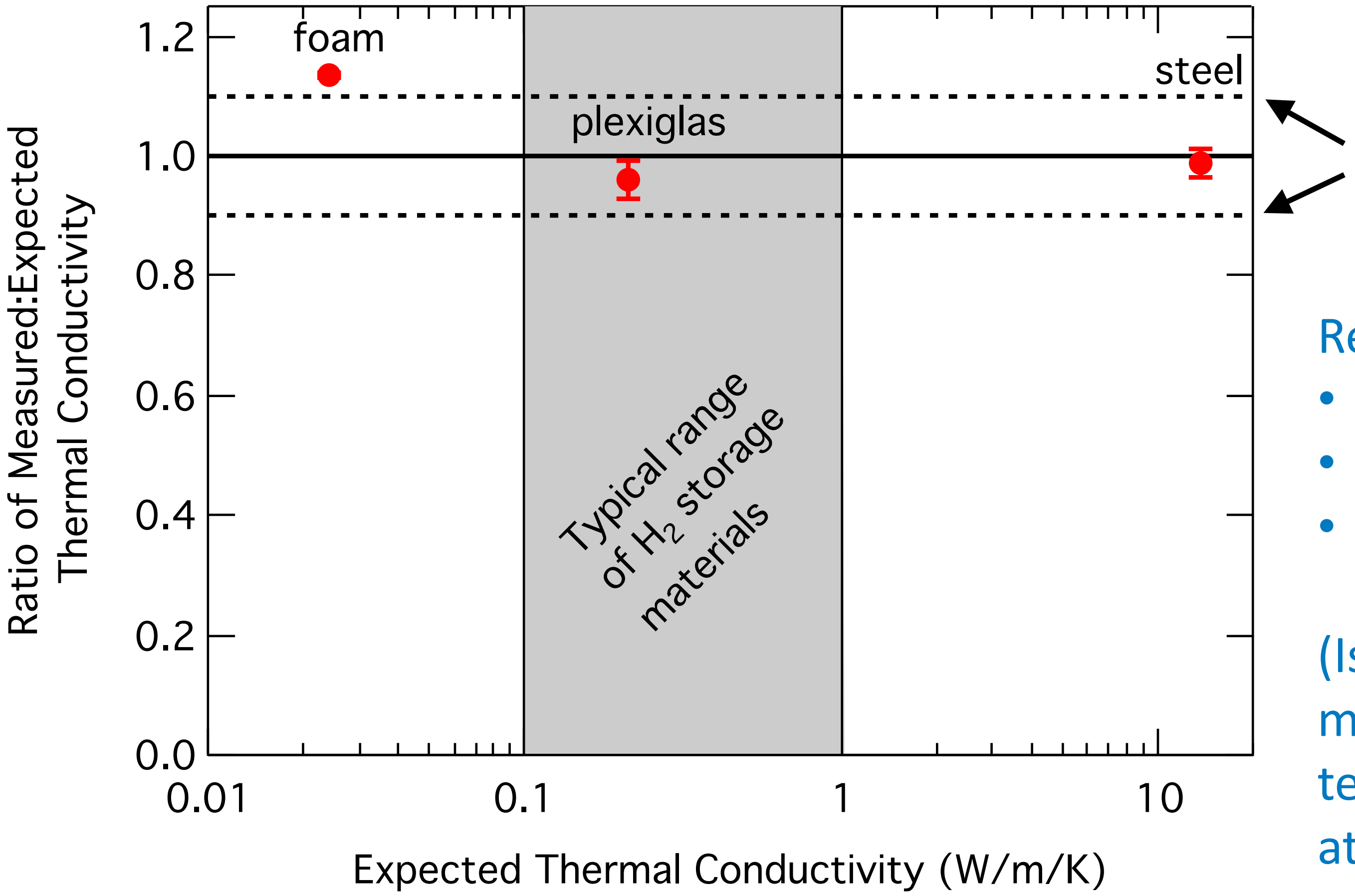
Cryostat temperature controls

Pneumatic valves

Cryostat

Accomplishments: Validated Measurements

Validated the accuracy of the apparatus with 3 reference materials.



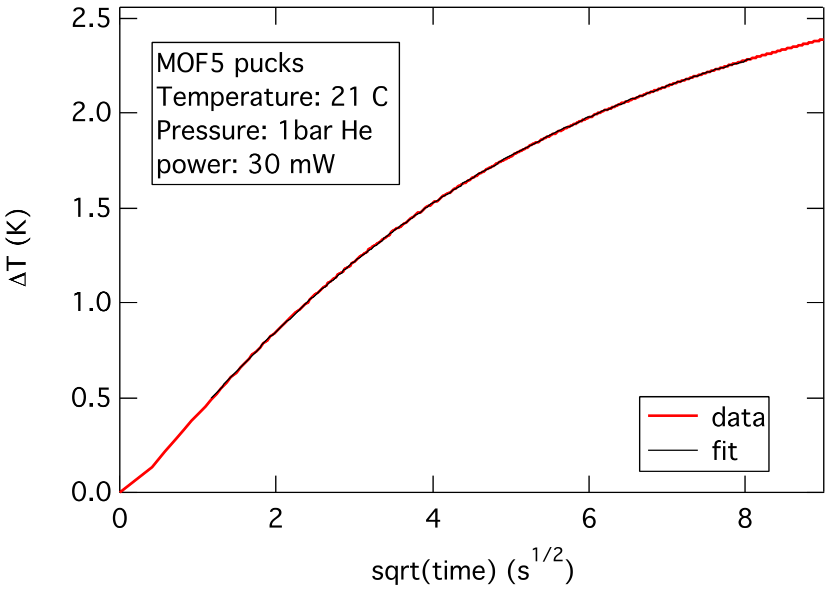
Reference materials:

- Stainless Steel
- Plexiglas
- Foam Insulation

(Isotropic measurements at room temperature, atmospheric pressure)

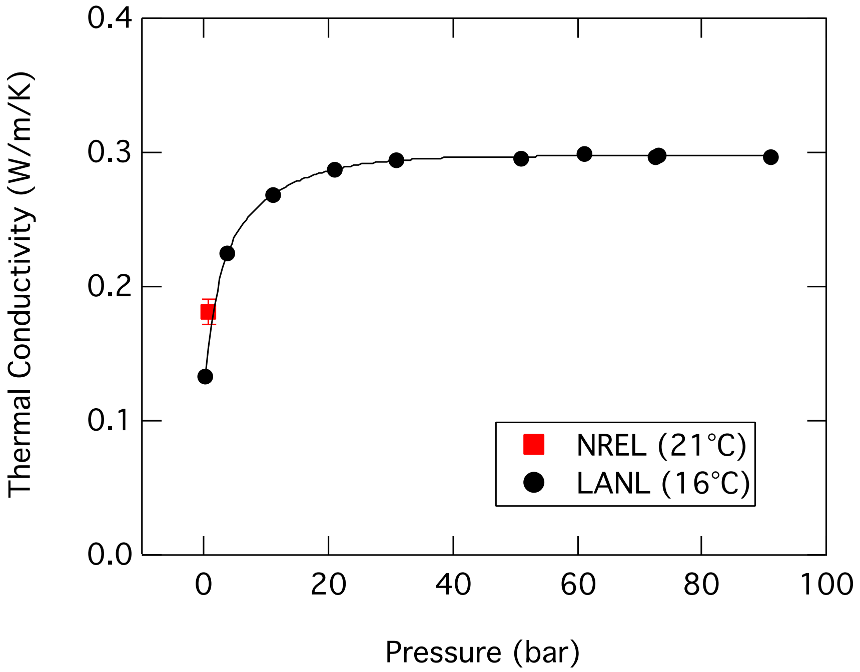
Good agreement over 3 orders of magnitude

Accomplishments: MOF 5 Measurement



In collaboration with Troy Semelsberger (LANL), we have measured MOF5 pucks:

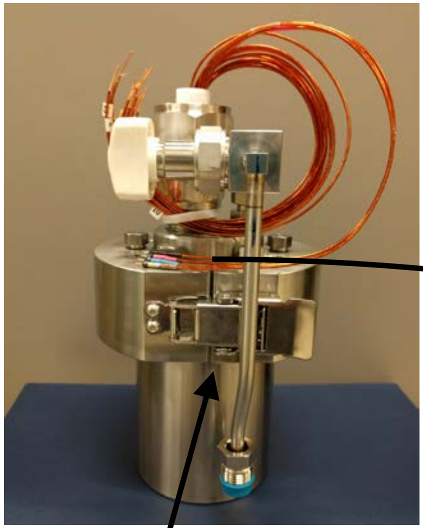
- 5cm diam x 1.3 cm
- Density = 0.4g/mL
- Room temperature
- He at ~1 bar
- Isotropic measurement



Good agreement in sorption material measurements.

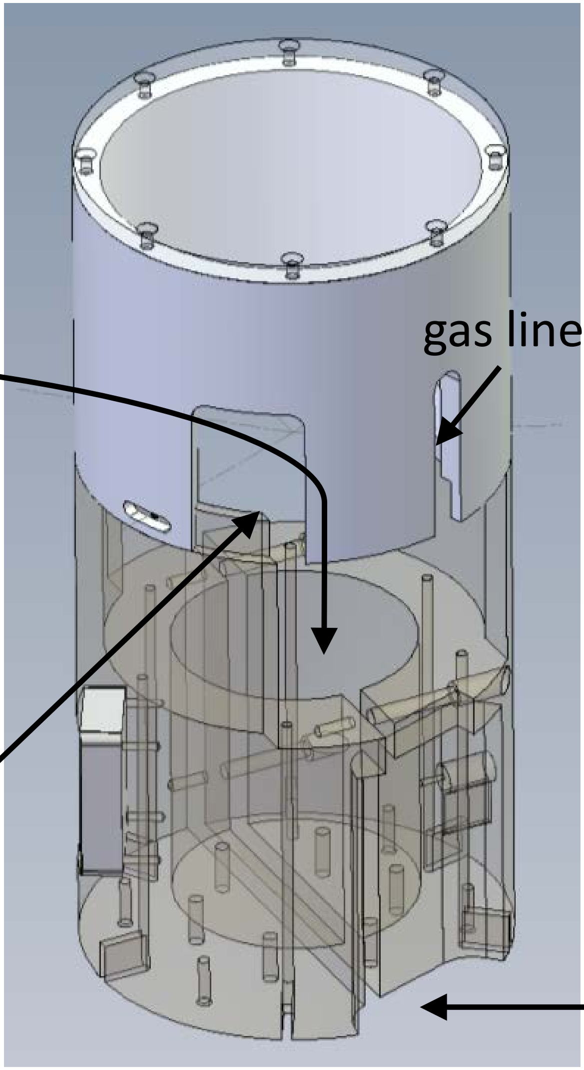
Accomplishments: Fabricated Isothermal Shroud

Pressure vessel



sample and sensor inside

notch for
valve knob



gas line port

cutout for gas
line connection

Shroud and pressure
vessel mounted atop
cryostat

The shroud will ensure isothermal temperature profile of samples.

Accomplishments: Cryogenic Measurements

We have demonstrated thermal conductivity measurements at cryogenic temperatures using BK glass samples (satisfies milestone).

T (K)	Gas	Pressure (Torr)	K Measured (W/m-K)	K Accepted (W/m-K)†	Percent Deviation
75.6	He	615	0.47	0.45	+4.4%
75.6	He	210	0.46	0.45	+2.2%
295	He	615	1.15	1.1	+4.6%
295	Air	615	1.12	1.1	+1.8%

- Measured values are well within the required 10% of accepted values.
- Additional investigation is needed to determine error bars for measured values.

† Ekin J 2006 *Experimental techniques for low-temperature measurements* (Oxford: Oxford University Press)

Remaining Challenges and Barriers: Thermal Conductivity

- **The Single-Sided Transient Plane Source models will require experimental validation.**
- **Ensuring hydrogen saturation of samples**
  - The current design allows hydrogen to enter through the top of the module. Dense samples may prevent hydrogen from percolating through the entire sample.
- **Providing uniform compression of powders.**
  - Powder measurements will require a membrane that is permeable to hydrogen, but not to the powder.

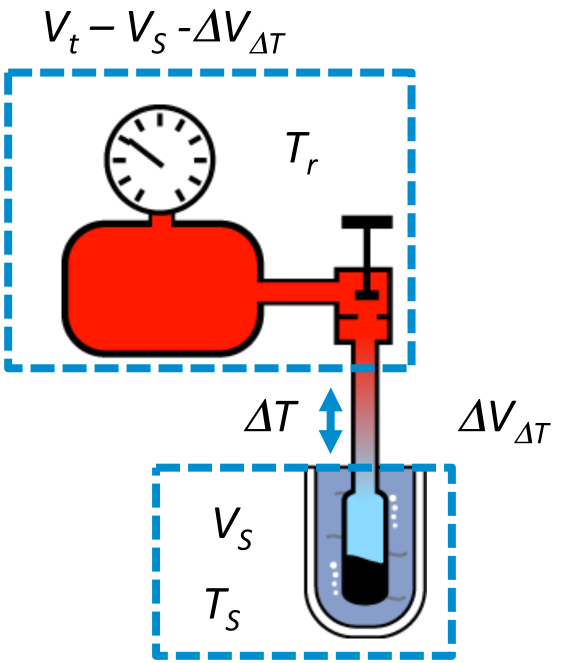
Proposed Future Work: Thermal Conductivity

- **FY16—Validate the apparatus for pressure and powders.**
  - Validate the apparatus with pressurized He and H_2.
  - Develop hardware and test protocols for measuring powder samples.
  - Fully automate instrument so that unattended measurements can be made at various pressures and temperatures.
- **FY17—Assist materials-research groups to characterize and validate their samples.**
  - Measure external samples at NREL.
  - Validate materials properties claims on novel materials.
  - Conduct studies to determine the effects of cycling on the thermal properties of promising hydrogen storage materials.

Relevance: Measurement Validation & Error Analysis

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 validate their samples sorption capacities for hydrogen-storage.
  - -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 experimental procedures to minimize such errors.
  - -Analyze materials for chemical reaction by-products.

Accomplishments: Measurement Validation

- **Milestone: Worked with groups funded by DOE to validate measurements and analyze results.**
  - 2 groups with 2 samples (39 measurements total)

    (Measurements include TPD, PCT, BET etc.)
  - Reported the results to DOE.

    (Data is considered proprietary and cannot be shared.)
- **Collaborated with groups for discussion of error analysis and advisement on protocols to enhance accurate measurements.**
  - 2 groups

Accomplishment and Progress: Inter-laboratory Volumetric Capacity Hydrogen Adsorption Measurement Study

Milestone:

In recognizing the increased importance of *volumetric capacity* as a crucial metric for hydrogen storage materials, this study compares H_2 *volumetric capacity determinations* on two distinct sorbent samples measured at 77K and ambient temperature from different laboratories to gauge what variations typically exist among laboratories.

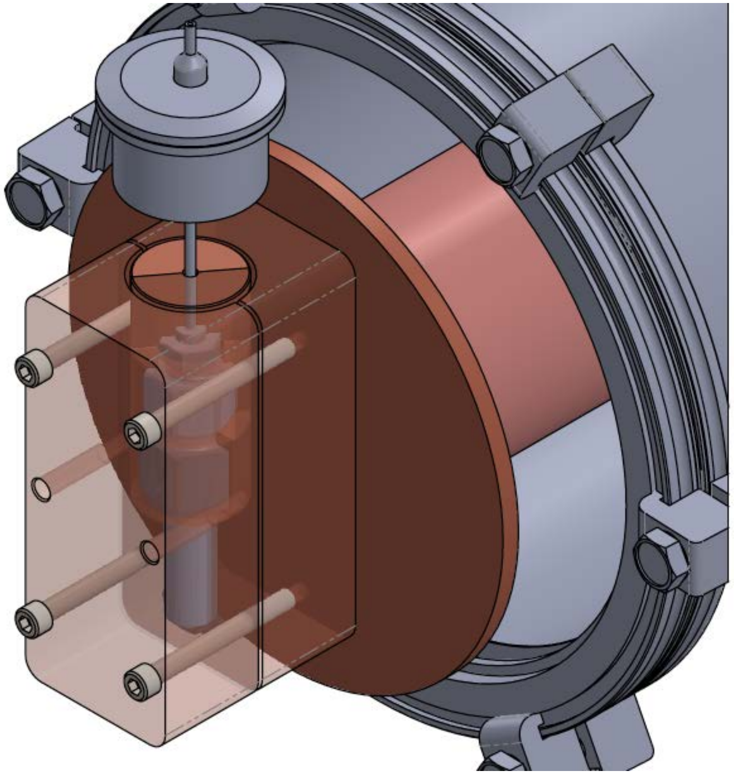
- Includes determinations of excess and total volumetric capacities
- Builds on smaller previous study focused on excess gravimetric capacity

  (K.E. Hurst, P.A. Parilla, K.J. O'Neill, T. Gennett *Appl. Phys. A* 122; 42, 2016.)
- 5 grams of each material were distributed to participants in February 2016
- Detailed instructions were provided to each participant including:
  - degas conditions for each sample
  - measurement methods for the volume of the sample
  - recommended calculations for determining the capacities
- 15 confirmed participants (including NREL)
  - USA, International (Europe, Asia), IEA-HIA
    - academia, national laboratory, industry

This NREL-led hydrogen-storage study will assess the accuracy of excess and total volumetric capacities measurements within the hydrogen storage community. Knowledge of the measurement accuracy enables meaningful comparison of the sorption capacities.

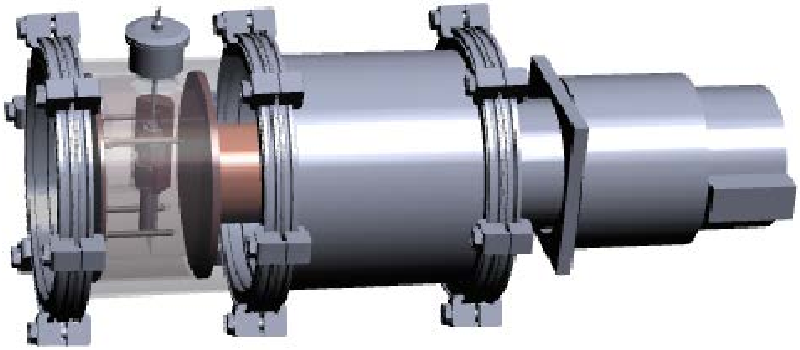
Accomplishments and Progress: Variable Temperature PCT Cryostat Design

Progress toward Milestone



Modification of one of our current PCT instruments includes a cryo-cooler for controlling the sample temperature from 50K to 350K.

This requires a new design for the sample holder, cyro-cooler configuration and software development.



The design of the variable temperature PCT instrument will expand NREL's characterization capabilities to include volumetric measurements from 50K to 350K and enable the facile determination of the heat of adsorption.

Proposed Future Work

- **Validate measurements for hydrogen sorption.**
  - Need to validate 2 samples (FY17)
- **Analyze data and publish results from the inter-laboratory volumetric hydrogen capacity measurement study.**
- **FY17: Develop new capabilities for measuring the hydrogen sorption with increased temperature range (50K – 300K).**
  - Development of system in progress.
    - Finalize design of cryostat and sample holder for PCT system
  - Develop new LabVIEW instrument software
  - Validate isosteric heat of adsorption measurement
  - This capability will allow facile determination of the isosteric heat of adsorption

NREL Characterization Milestones

NREL Core Capability Milestone Name/Description	End Date	Type
1. Initiate, with a minimum participation level of 5-laboratories, experimental determination of the gravimetric and volumetric capacities of an agreed upon standard sorbent material. Participant laboratories may include international collaborators.	12/31/2015	Regular **(100% complete)**
2. Demonstrate low temperature (<100K) experiment capability on the Variable-Temperature Thermal Conductivity apparatus for a standard whose thermal conductivity values are within the 0.1-2 W/m/K expected range for initial hydrogen sorbent materials. Results will be within 10% of accepted value.	3/31/2016	Regular **(100% complete)**
3. Thermal conductivity apparatus Lab View programming completed and system ready to evaluate samples for DOE. Demonstrate thermal conductivity measurements at 3 temperatures between 77K and 358K for an agreed upon sorbent standard. The thermal conductivity of the sample will be measured to within 10% of the accepted value.	6/30/2016	SMART **(90% complete)**
4. Measure and validate the gravimetric capacity, volumetric capacity and thermal conductivity of 2 samples as assigned by DOE. Submit full report to DOE within 30 days of completion of analysis	9/30/2016	Regular **(50% complete)**

NREL Characterization Initiatives

- **PCT Analysis: Upgrade a commercial Sieverts instrument, a PCTPro 2000, with a cryo-cooler to allow for variable sample temperatures for PCT measurements at arbitrary temperatures from ~50 K to 350 K and pressures up to 160 bar hydrogen. This is a FY17 activity.**
  - Allow measurements for determination of the hydrogen isosteric heats of adsorption.
  - Facilitate determining the parameters of universal isotherm equations such as the Dubinin-Astakhov (DA) model.
  - Allow for desorption at specific temperatures for quantification of sorbed hydrogen at specific temperatures. (For materials with multiple binding sites)

- **Thermal Conductivity and Heat Capacity. Measure the thermal properties of the sorbent and hydride materials used for hydrogen storage. This is a FY16 activity.**
  - Allow for the measurement of the thermal conductivity of hydrogen storage materials at temperatures from 77K to 400K, and gas overpressures up to 100 bar,
  - Be able to measure materials ranging from loose powders to packed powders to densified pucks.
  - Both the pressure and temperature will be computer controlled, allowing one to establish a preset matrix of temperatures and hydrogen pressures at which to perform measurements.
  - Evaluation of three-dimensional heat flow.
  - Evaluation of thermal diffusivity in order to calculate heat capacity
  - Allow for expansion/contraction of materials for multi-cycle sorption/desorption TC experiments.

NREL Team

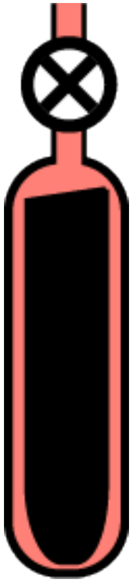
- Rory Andrykowski – Mechanical design & drafting
- Jeff Blackburn – Nanomaterial synthesis
- Arrelaine Dameron – Chemical synthesis & analysis
- Mira Dimitrievska – (NIST) Diffraction & scattering
- Sue Ferrere – Chemical synthesis
- Tom Gennett – NREL's H_2 Storage Program Lead
- Katie Hurst – H_2 sorption measurements & data analysis
- Michele Olsen – Thermal conductivity project lead
- Philip Parilla – Volumetric capacity protocol & error analysis
- Steve Robbins – LabVIEW programming
- Jacob Tarver – (NIST) Diffraction & scattering
- Jerry Tynan – Electronics & mechanical design

Technical Back-Up Slides

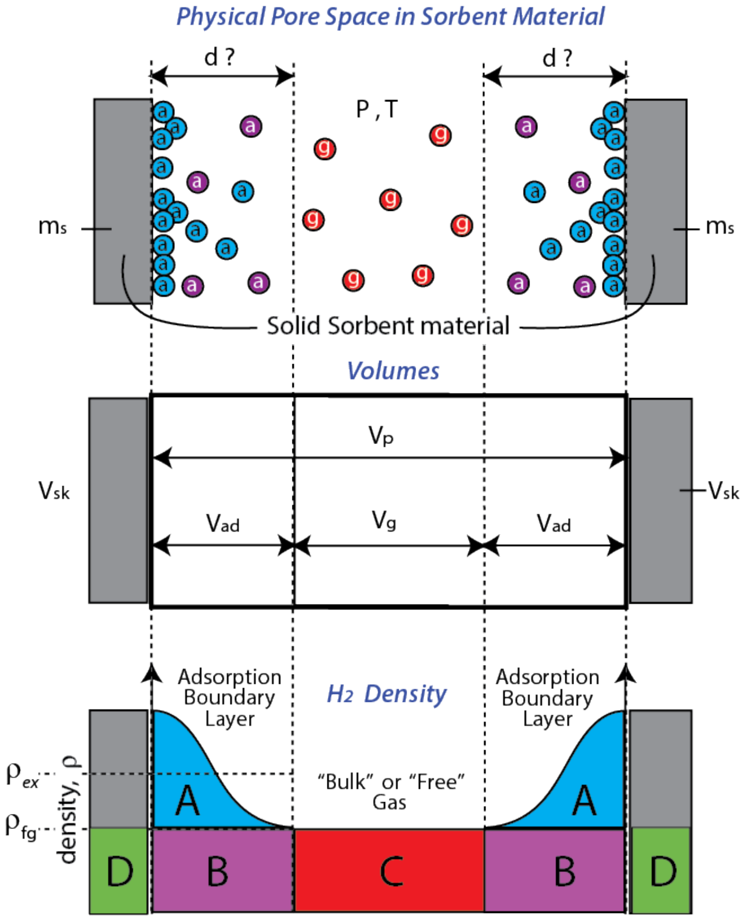
Approach: Accounting for the Hydrogen

Different ways to count H_2:
Excess, Net, Absolute, Total

$$\Lambda_{VC} = \sum_i m_{i\,H_2} \Big/ \sum_i V_i$$



Critical To Not Double-Count the Hydrogen!!!



TERMINOLOGY
Material "Excess" Capacity = (A)
Material "Net" Capacity = (A-D)
Material "Absolute" Capacity = (A+B)
Material "Total" Capacity = (A+B+C)

Adapted from Best Practices, K. Gross

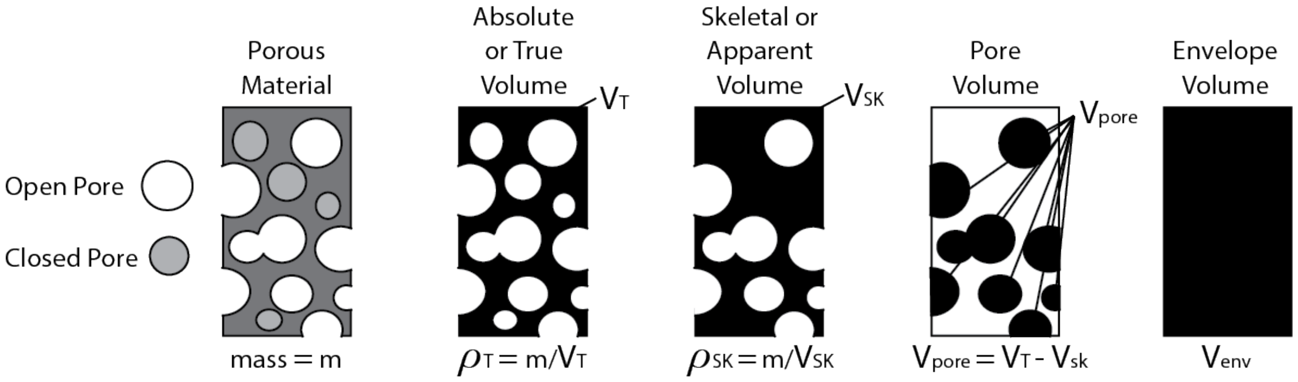
Approach: Defining & Accounting for the Volumes

There are various types of volumes to consider

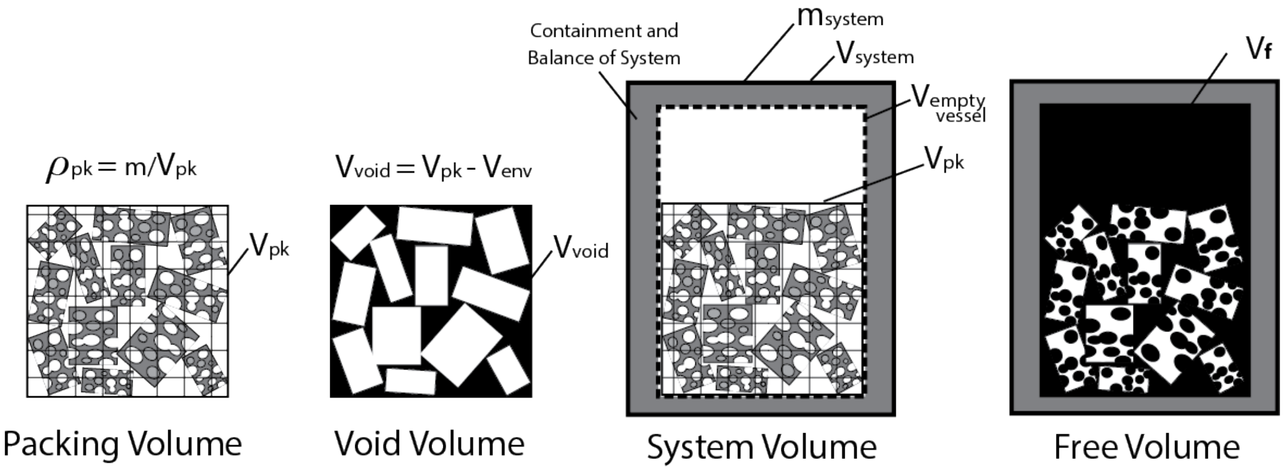
- It is critical that the volume chosen for a FOM can actually be determined in practice!

- The methodology for determining that volume must be explicitly specified.

A) Materials Level Definitions



B) Systems Level Definitions



Adapted from Fig. 84 of Best Practices, K. Gross

For more detail see: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage.pdf