Hydrogen Sorbent Measurement Qualification and Characterization

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National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

ST014

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

Overview

HySCORE

Timeline*

Project Start: 10/1/2015

End: Project continuation determined by DOE. Currently scheduled through 9/30/18

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

Budget

FY17: $1,444,792

FY18: $750,000

Total Effort: $3,625,000

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

Partners/Collaborators

NIST – Craig Brown, Terry Udovic
PNNL – Tom Autrey, Mark Bowden
LBNL – Jeff Long, Martin Head-Gordon
HyMARC – SNL, LLNL, LBNL
LANL, USA – Troy Semelsberger
H2Technology Consulting, USA – Karl Gross
H_2ST^2, USA – Hydrogen Storage Tech Team
University of Delaware – Eric Bloch
Thesis Corporation – Justin Lee
Univ. Wyoming – Bruce Parkinson
Ford – Justin Purewal, Mike Veenstra

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Relevance: HySCORE Project Objectives

HySCORE

An NREL-led National Laboratory collaboration and synergistic research effort between:

NREL, LBNL, PNNL, NIST

- To ***Develop*** and ***Enhance*** Hydrogen Storage Core Capabilities, i.e. Characterization Techniques
- To ***Validate*** claims, concepts, and theories of hydrogen storage materials
- To ***Double*** hydrogen storage energy density (increase from 25g/L to 50 g/L)

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NIST Center for Neutron Research

Relevance: Overall Validation/Characterization Efforts

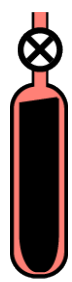
- **Validate hydrogen capacity claims for DOE**
  - Measure "champion" samples from DOE grant awardees
- **Promote valid comparisons of hydrogen-storage materials and decrease irreproducibility due to errors**
  - Provide uniform and well-defined metrics for comparisons
  - Understand sources of common errors and how to mitigate them
  - Establish volumetric capacity protocols
- **Conduct inter-laboratory comparison for volumetric capacity measurements**
  - Analyze actual implementations of protocols and variations thereof
  - Provide feedback to participants on errors and discrepancies
- **Develop variable-temperature PCT capability**
- **Establish *in situ* thermal conductivity measurements**

Relevance/Approach: Volumetric Capacity Measurements

Relevance:

- **Volumetric capacity metrics are critical**
  - Must be uniform, consistent, and unambiguous
  - Established protocol for determining and reporting
- **Goal: double the capacity over 700-bar tanks**
  - Move towards ~50 g-H_2/L.





Approach:

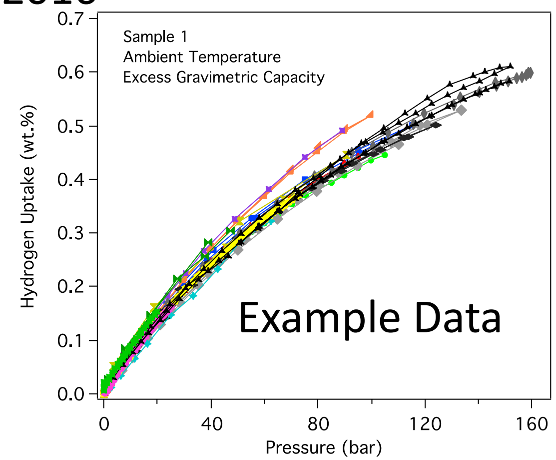
- **Compare volumetric capacity (VC) measurements with inter-laboratory comparison**
  - Organize and manage an inter-laboratory comparison (ILC18) on the hydrogen capacity measurements of 2 standard samples.
  - Analyze the data to discern sources leading to variations of the results, common errors, and misunderstandings.
  - Report on these findings to the scientific community.
  - Based on previously established protocols.(Parilla, et al, Appl. Phys. A, 2016).

Accomplishment: ILC18 Manuscript Finished

- **Manuscript completed and under internal review**
  - Send to participants for review
  - Submit for publication to Energy and Environmental Science

- **Goal: Study and Understand Variability in Volumetric Capacity Determinations**
  - Two sample types: pellets and powder
  - Two targeted temperatures: "Ambient" and liquid nitrogen
  - Includes determinations of 3 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 sent 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 the capacities
  - 13 confirmed participants (including NREL)
  - USA, International (Europe, Asia), IEA-HIA
  - academia, national laboratory, industry



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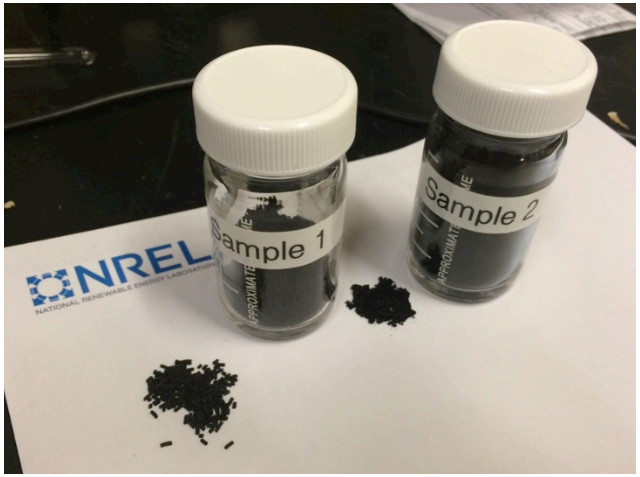
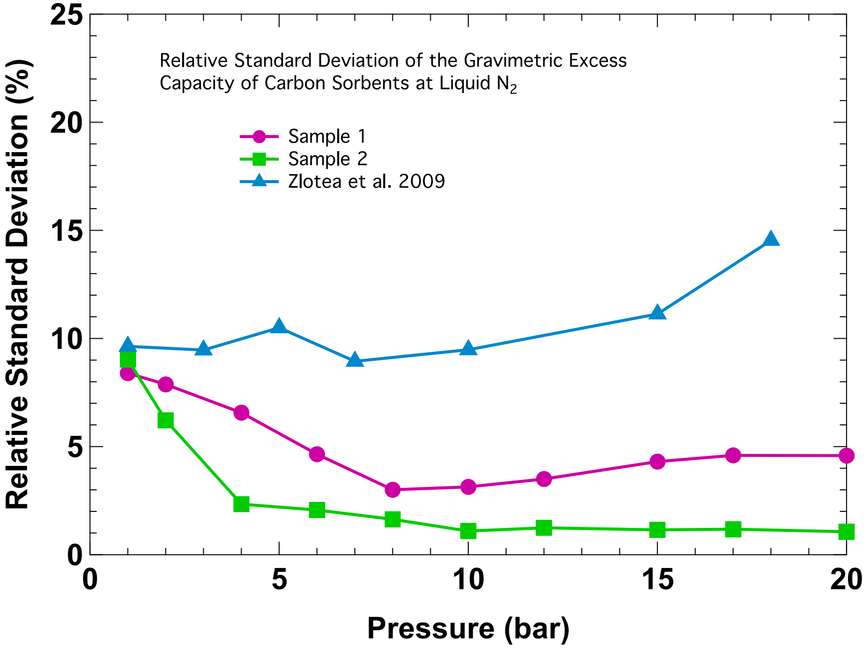
Accomplishment: ILC Data Analysis

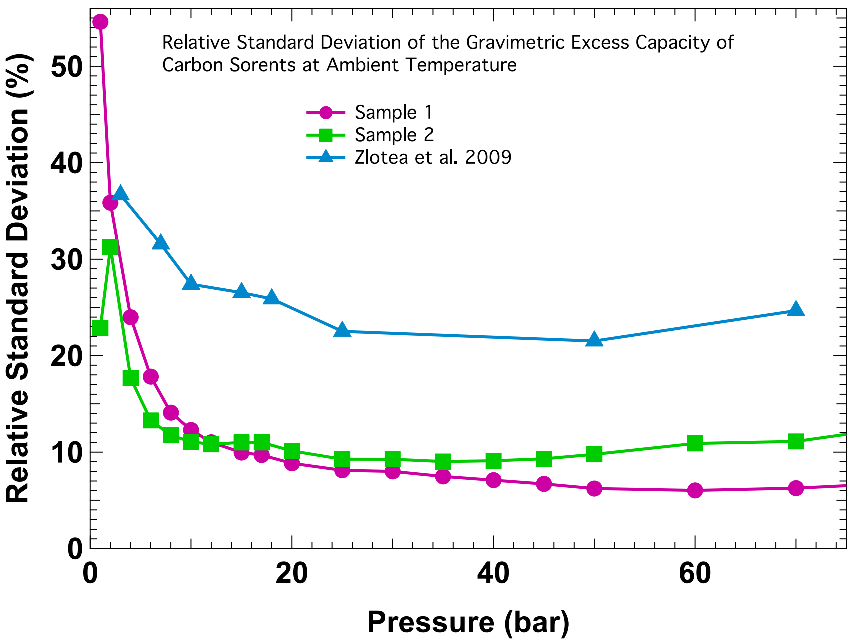


- **Data Received:**
  - 14 data sets at ambient conditions Sample 1
  - 13 data sets at ambient conditions Sample 2
  - 10 data sets at liquid N_2 data Sample 1
  - 9 data sets at liquid N_2 data Sample 2
  - Data from 13 participation laboratories including:
    - 1 industry, 8 government, 4 academic labs.
    - 9 US, 4 international institutions
    - 12 manometric instruments, 1 gravimetric instrument
    - Participants have been notified of their results
- **Data Analysis:**
  - Data received was inspected and investigated for gross errors
  - Gross errors from misunderstandings, experimental failures, or miscalculations were revisited and corrected by participants
  - Isotherms were interpolated to a common set of pressures to allow statistical analysis
  - General analysis is completed. Additional analyses are in the initial stages; correlations will be investigated, conclusions drawn and results will be published

Analysis: Relative Standard Deviation Comparison

Data show that it is possible to have good reproducibility





- Excess gravimetric capacity comparison of a previous study with this study (ILC18)
- Zlotea et al. study included data only if the adsorption was reversible
  (if desorption was +/-20% of the adsorption amount)
  included 9 data sets out of 11 – 77K (eliminated 2)
  included 10 data sets out of 12 – ambient conditions (eliminated 2)
- ILC18 has included all data sets for analysis

C. Zlotea et al. Int J Hydrogen Energy 2009; 24, 3044

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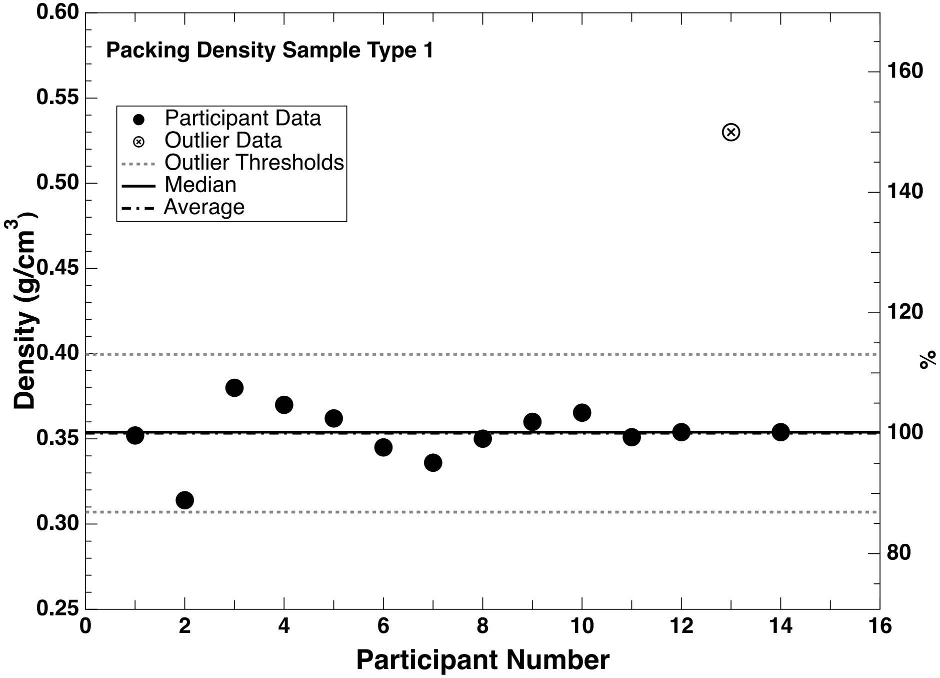
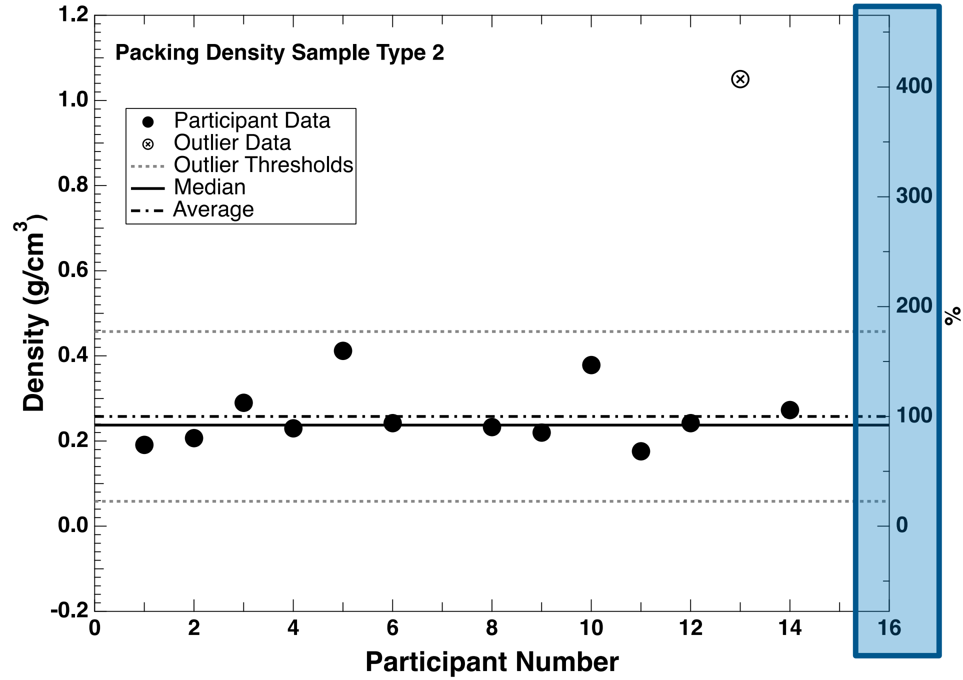
Analysis: Packing Densities Impacted Volumetric Capacities

Sample Type 1



Sample Type 2



Volumetric Total Capacity

$$\Lambda_{tp} = \frac{m_{tot\ H}}{V_{pk}}$$

Volumetric Excess Capacity

$$\Lambda_{ep} = \frac{m_{ex\ H}}{V_{pk}}$$

- Powder sample, Sample 2, has a much higher variability in packing density than pelletized material, Sample 1.
- Participant 13 considered an outlier for volumetric capacities
- The variation in packing density directly affects the total and excess volumetric capacities

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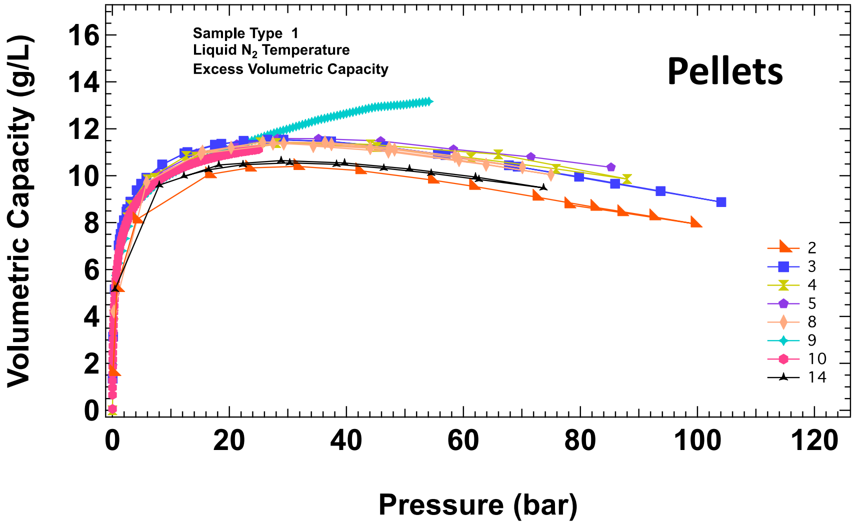
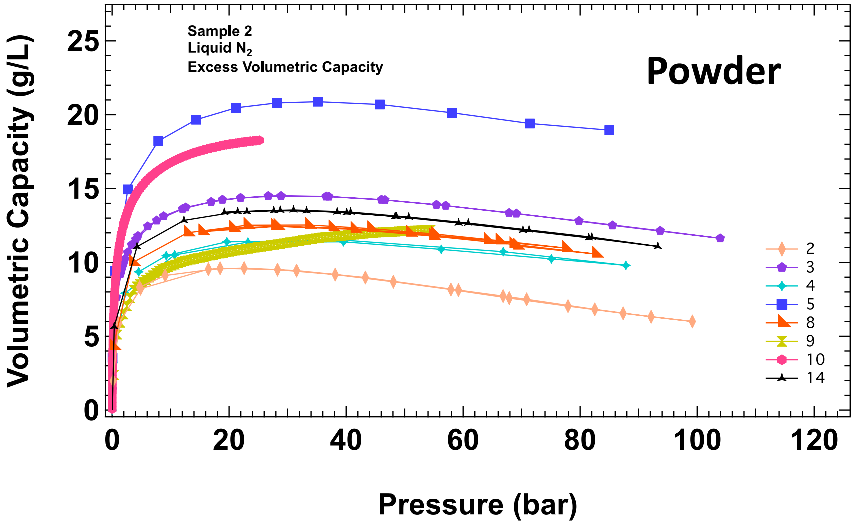
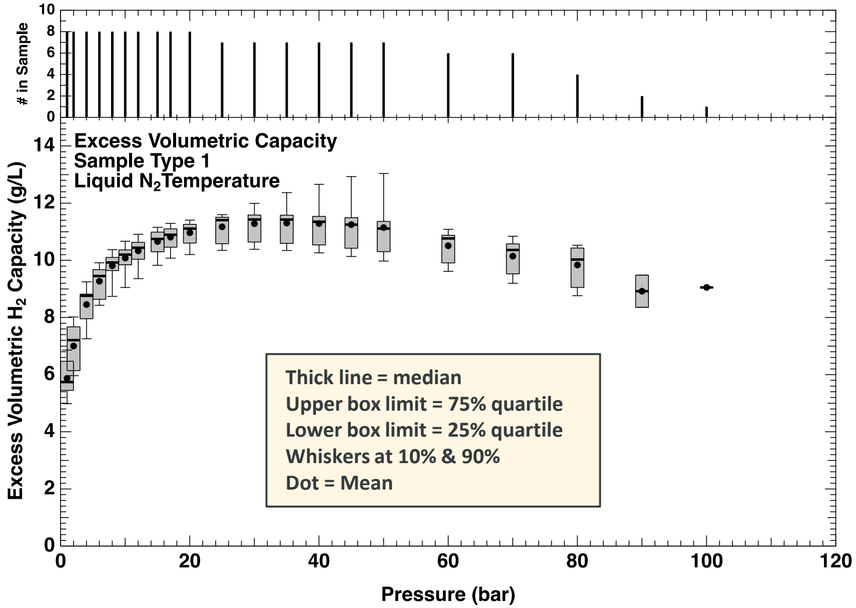
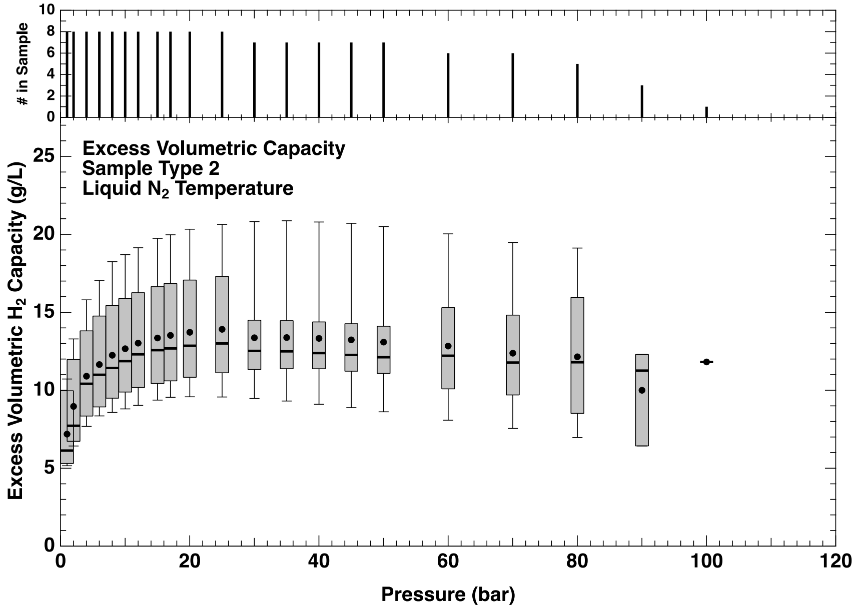
Analysis: Excess Volumetric Capacity – Liquid N_2

Variation in Packing Density Causes Isotherm Variability



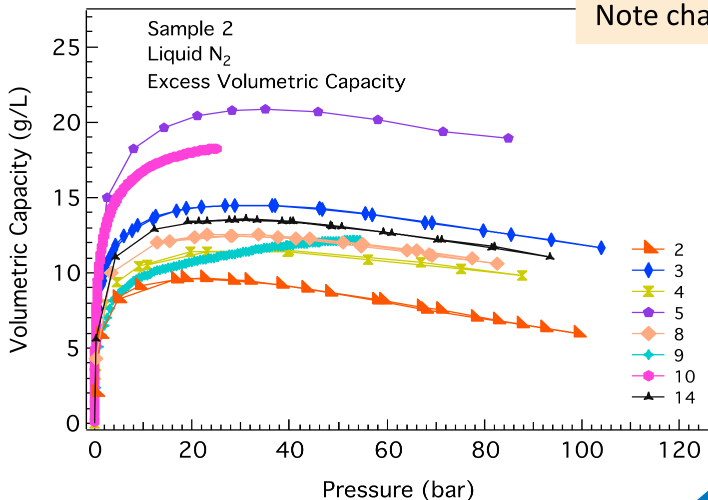




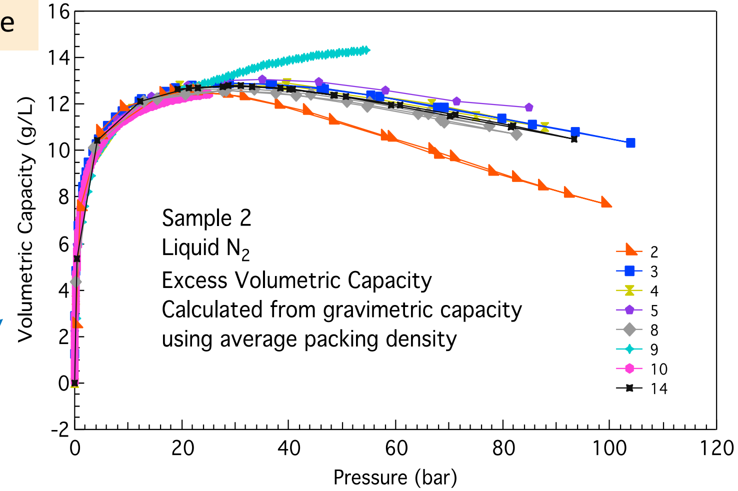


Analysis: Excess Volumetric Capacity - Liquid N_2

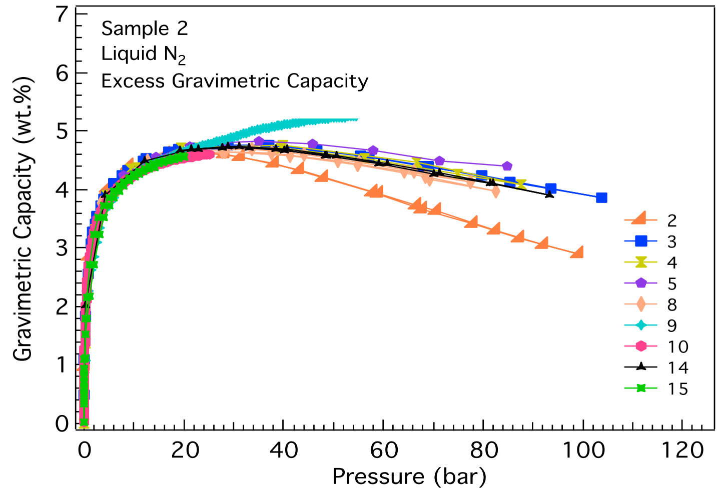
Normalizing to average density reduces spread



Note change in y-axis scale



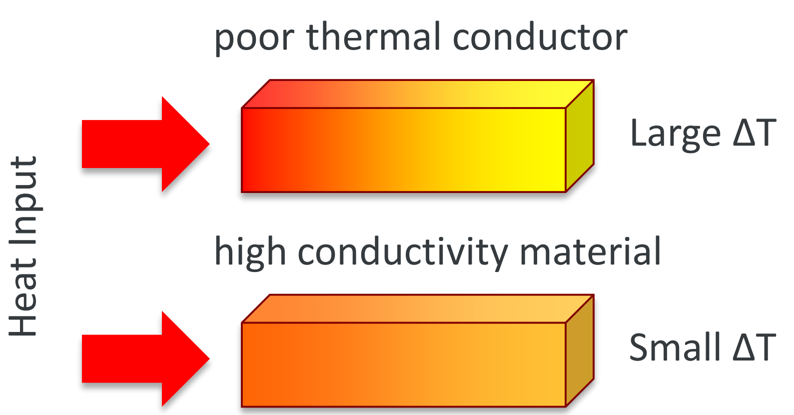
- Re-normalizing each excess volumetric capacity by the study's average packing density shows less scatter.
- The variability in the data becomes the same as that of the gravimetric excess measurement and is greatly reduced.
- This emphasizes the importance of how the packing density is determined



Relevance/Approach: Thermal Conductivity Characterization

Relevance:

- **Thermal conductivity properties of H_2-storage materials is a critical engineering issue for developing H_2-storage systems.**
- **Thermal conductivity measurements for H_2-storage materials must accurately be determined under relevant operating conditions.**
- **Centralize this capability so it is available for the DOE H_2-storage program both as a resource and as a verification facility.**



Approach:

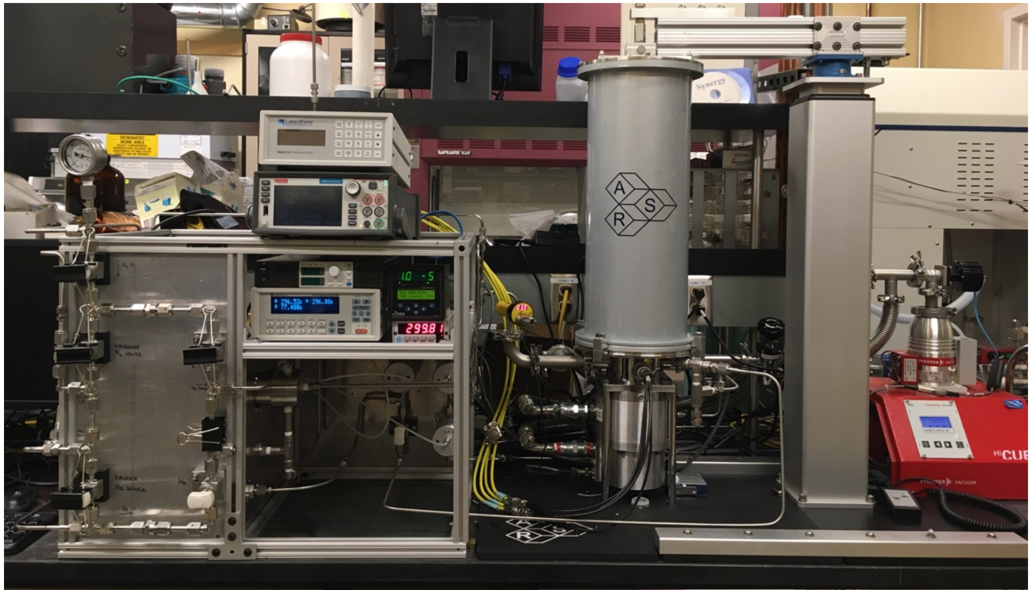
- **Develop thermal conductivity measurement apparatus for hydrogen storage materials from 40K to 375K, and at pressures up to 100 bar.**
    - Establish methodology for characterizing materials with different form factors.
    - Validate measurement technique over entire temperature and pressure range.
- **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.

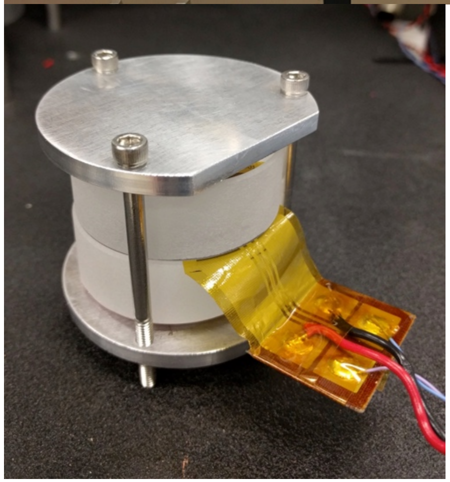
Accomplishment: Thermal Conductivity Apparatus

The system measures the effective thermal conductivity of a "composite" consisting of a sample plus a pressurized gas:

- **Gas: H_2, He (other gases possible)**
- **Gas Pressure: vacuum to 100 bar**
- **Temperature Range: 40 K to 375 K**
- **Sample types: solids & compressed pucks & powder**
- **Automation Completed**

(Red text: New for FY 18)





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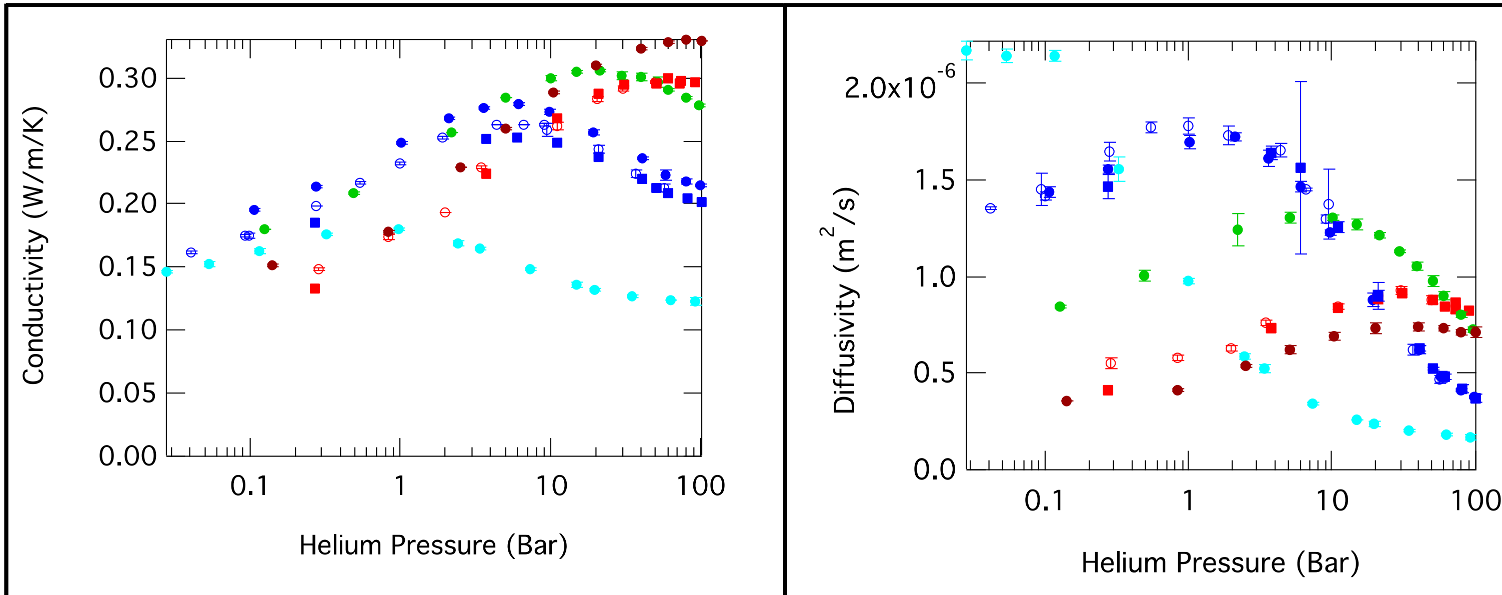
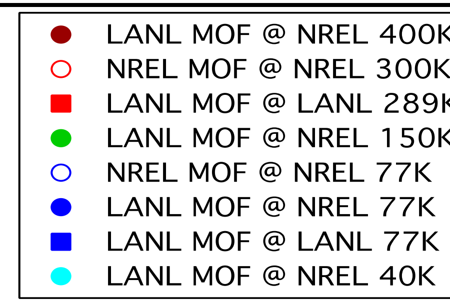
Accomplishment: MOF-5 TC Measurements

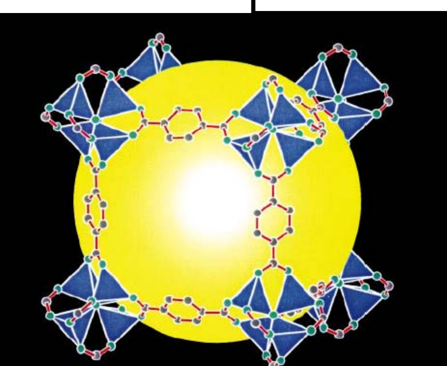
(In collaboration with Troy Semelsberger, LANL, Material from Mike Veenstra, Ford)

Thermal conductivity of MOF-5 in helium
as a function of pressure at different temperatures.





Helium shows anomalous behavior with pressure – very reproducible but not understood.

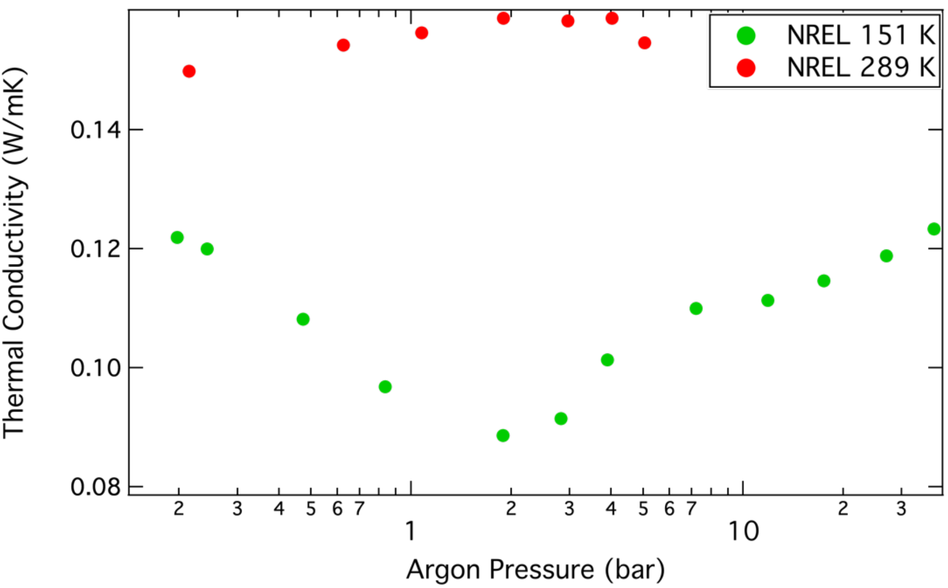


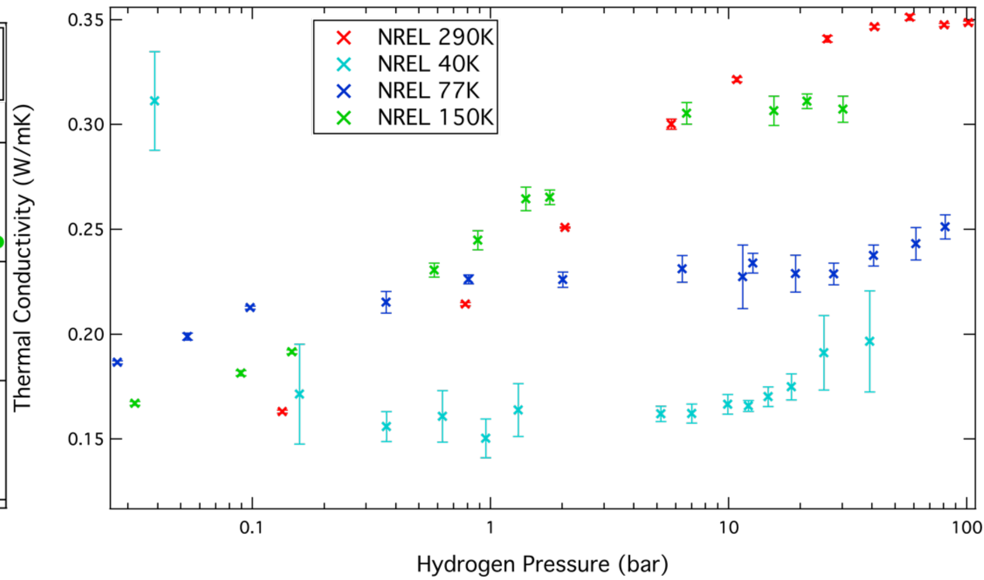
One cavity in the $Zn_4(O)(BDC)_3$, MOF-5, framework

Accomplishment: MOF-5 TC Measurements

(In collaboration with Troy Semelsberger, LANL, Material from Mike Veenstra, Ford)

Thermal conductivity of MOF-5 in Ar and H_2 as a function of pressure at different temperatures.





- Data averaged over 3 - 10 data points at a given pressure
- Equilibration time between data points:

  30 min for 290 K and 150 K **60 min** for 150 K, 77 K, and 40 K
- Equilibration time when pressure is increased: 20 min – 1h (depends on T)
- Applied power: 1 - 5 mW
- Analysis guarantees $\Delta T < 1$ K a reduced time of $\tau < 1$ s

Accomplishment: TC of Powders

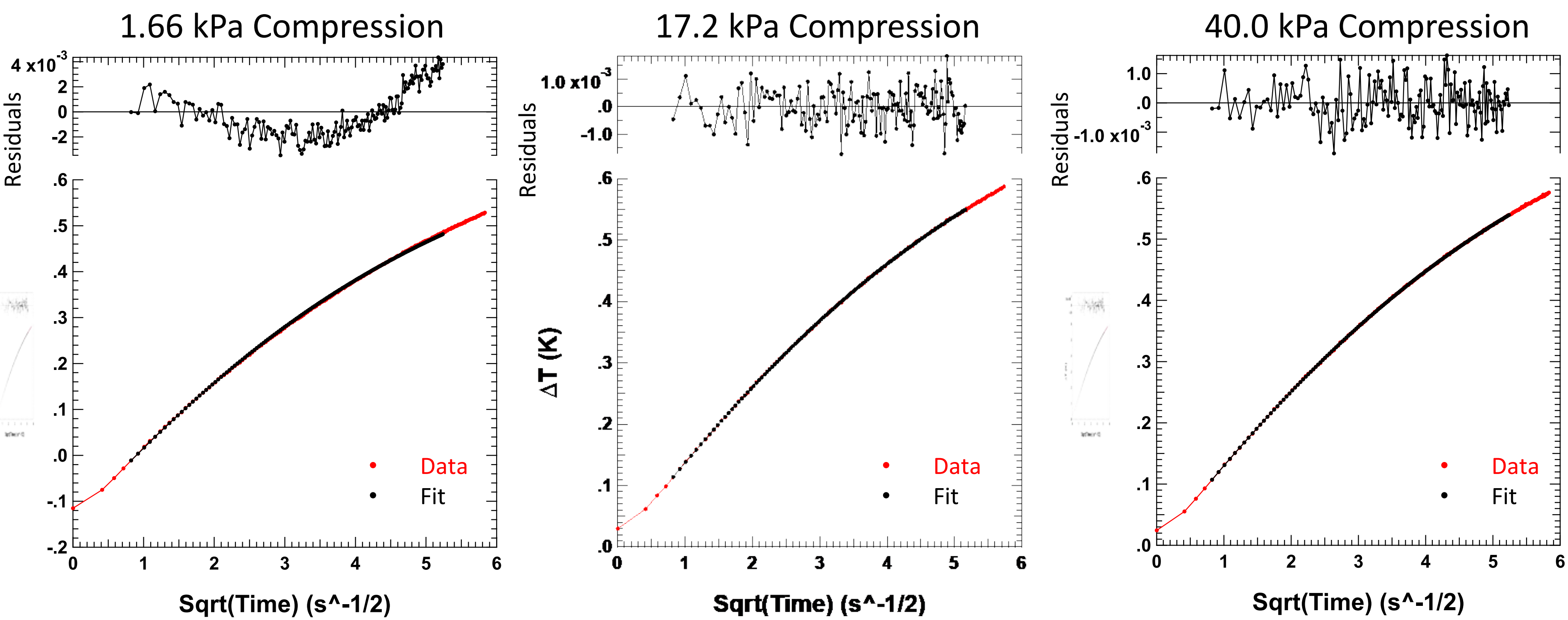
New Capability!

Sample holder

&

Loading Powder

Accomplishment: TC – Steel Powder Validation



Type 316-L Stainless Steel

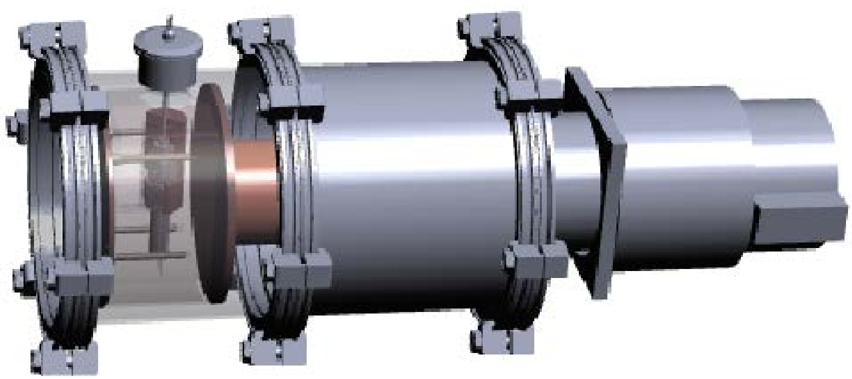
	NREL			Reference
Compression	1.66 kPa	17.2 kPa	40.0 kPa	
TC	0.18 $Wm^{-1}K^{-1}$	0.19 $Wm^{-1}K^{-1}$	0.20 $Wm^{-1}K^{-1}$	0.20 ± 0.02 $Wm^{-1}K^{-1}$
Gas	Air			N_2
Diameter	44 µm			35 ± 15 µm
Method	TPS			Hot-Wire

* Temperature calibrations are preliminary

Relevance/Approach: Continuously Variable Temperature PCT

Relevance:

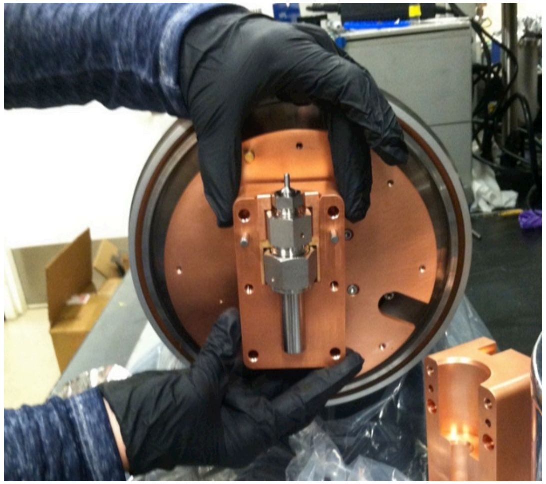
<u>DOE Objective:</u> To compete with 700-bar tanks, storage materials need to operate at reasonable temperatures approaching ambient and much lower pressures. Materials need to be tested at the expected operating temperatures and pressures.

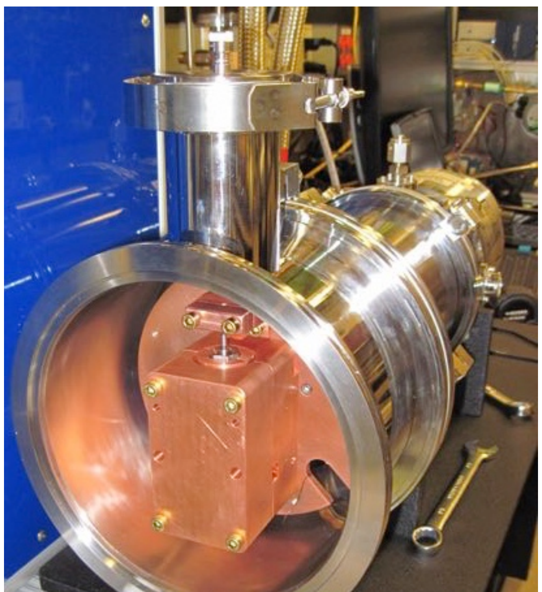


Approach:

- **Develop a continuously variable temperature PCT**
  - Will allow obtaining applicable Temperatures & Pressures
  - Must maintain exceptional accuracy
  - Commercial units suffer from non-uniform & unstable temperatures
  - Use high-capacity cryo-cooler with custom sample holder and thermal engineering
- **Steps**
  - Determine cryostat specifications & sample holder design ✓
  - Have cryostat & sample holder built ✓
  - Integrate hardware ←
  - Perform initial tests & measurements ←
  - Integrate software enhancements
- **Publish paper on design & performance**

Accomplishment: Continuously Variable Temperature PCT





- **Modified PCTPro 2000 instrument**
  - Pressures up to ~200 bar
- **Added cryocooler/cryostat**
  - Temperature: ~50K to 350K
- **Custom-made sample holder**
  - Copper temperature stabilizer
  - Stainless sample holder
  - Thermally designed to minimize temperature gradients at sample

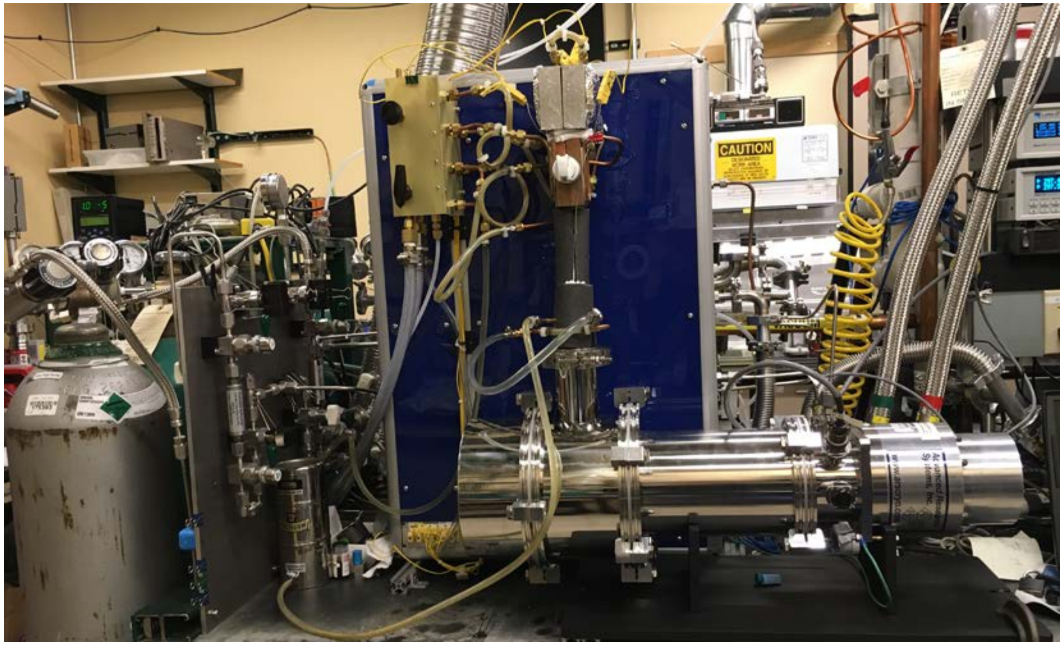
(Work performed in both FY17 & FY18)

Update: Variable Temperature PCT

HySCORE

- **Testing**
  - Verified operation of cryostat PCT instrument to produce accurate and reliable measurements
    - **Initial null measurements show good results**
      - **303K, 150K, 100K, 77K, 50K multiple times.**
  - **Cryo-cooler failed!**
    - Trouble started 10/10/17
    - Totally failed by 11/7/17
    - Warranty repair Jan. 2017
    - Received back March 2018
    - Re-installation in progress
  - Integrate new LabVIEW **software into instrument**
  - **Validate isosteric heat of adsorption measurements**

Cryostat was integrated with existing PCTPro 2000 that has been modified to improve thermal stability and uniformity.



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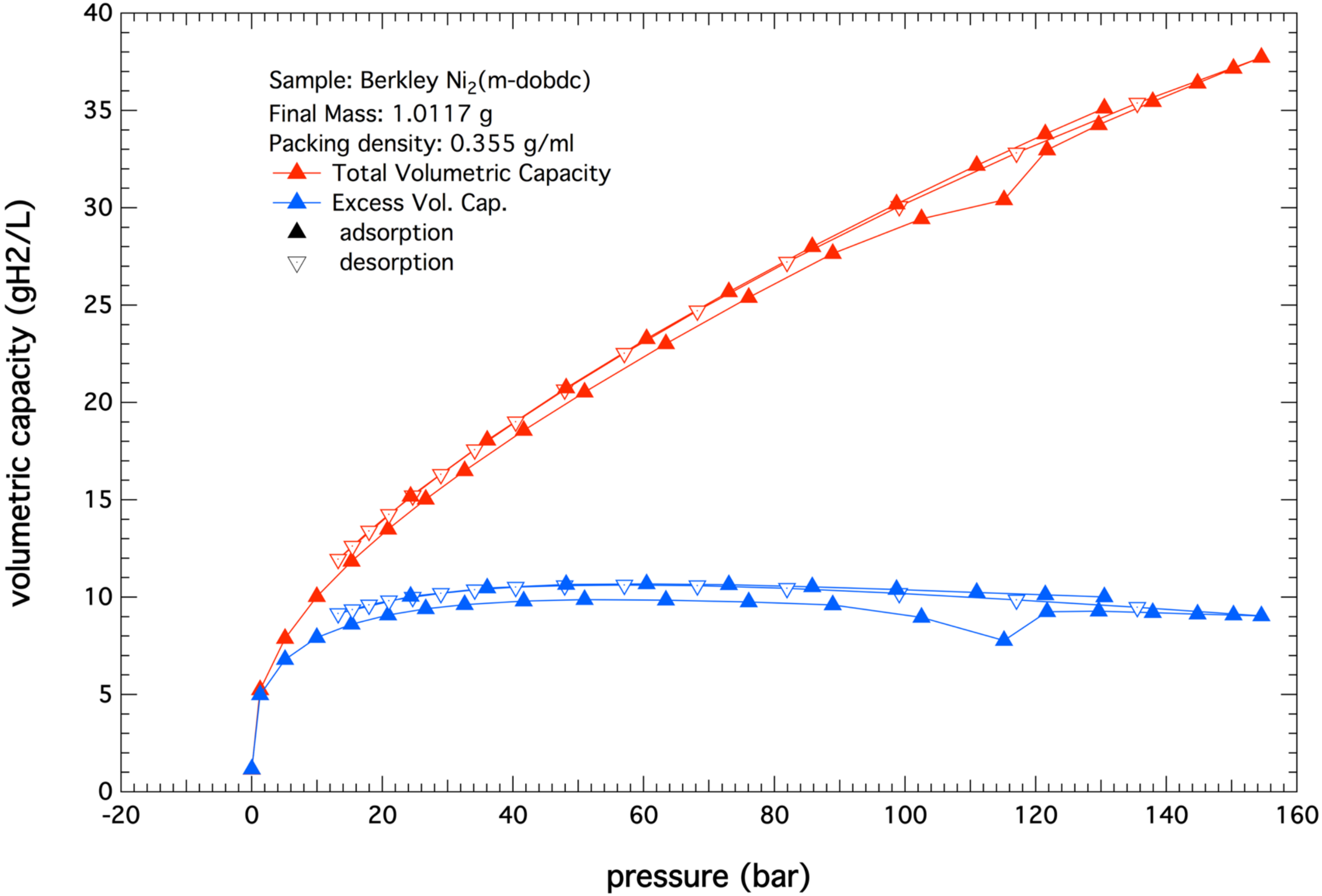
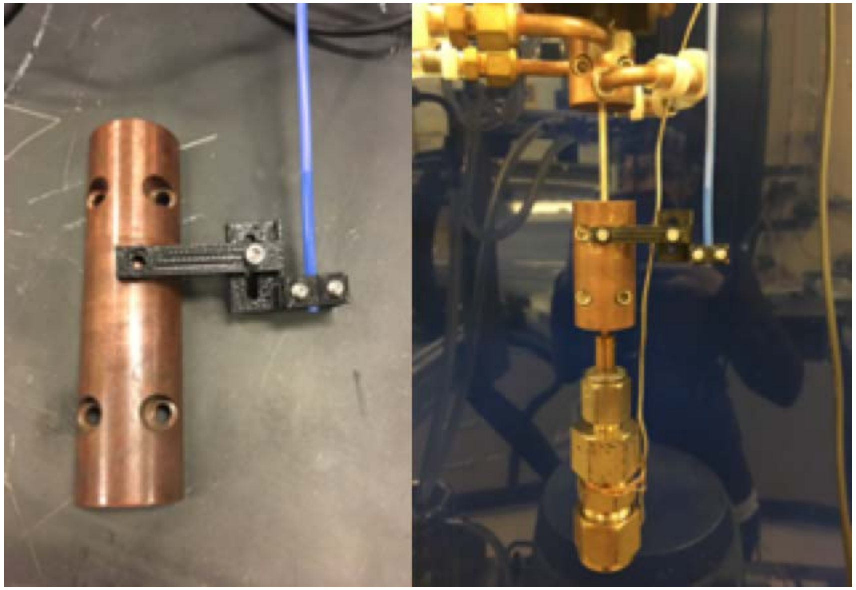
Accomplishment: LBNL Sample Measured at 100 K

Volumetric Capacity



Accomplishment: Automated LN_2 Refill



Autofill operation:

- Automated LN_2 refill apparatus utilizes a NORHOF #915 LN_2 Microdosing pump system.
- PT100 RTD sensor is inserted into the container at the desired level of the LN_2.

- Pump operates on a PID feedback loop with temperature feedback from the temperature sensor.

- When >-192°C, power is supplied to heaters dispensing LN_2 from the tube at the top of the pump head.

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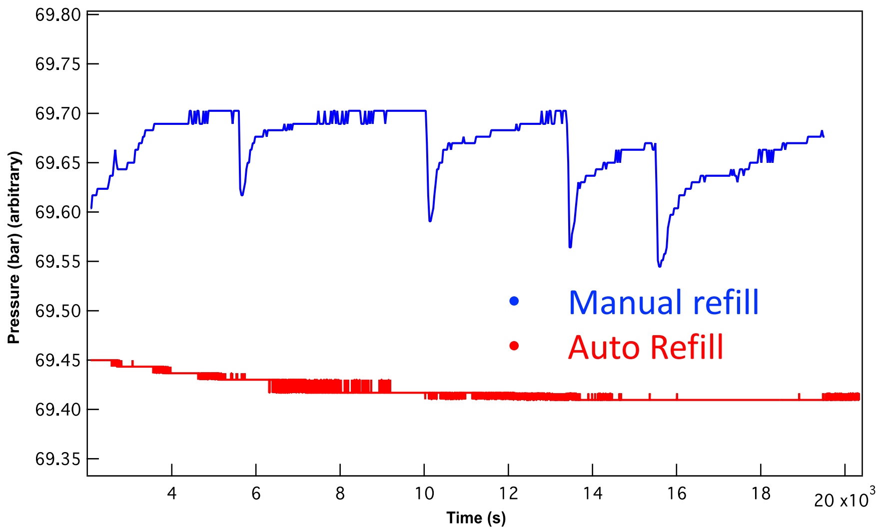
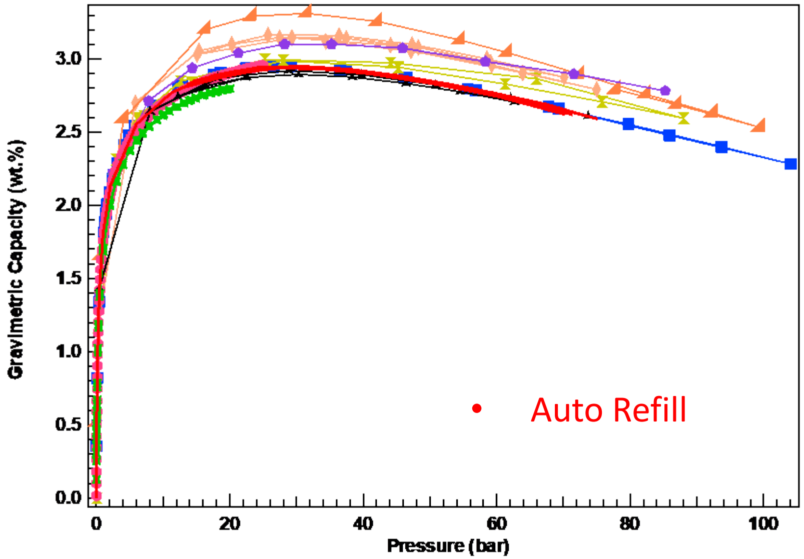
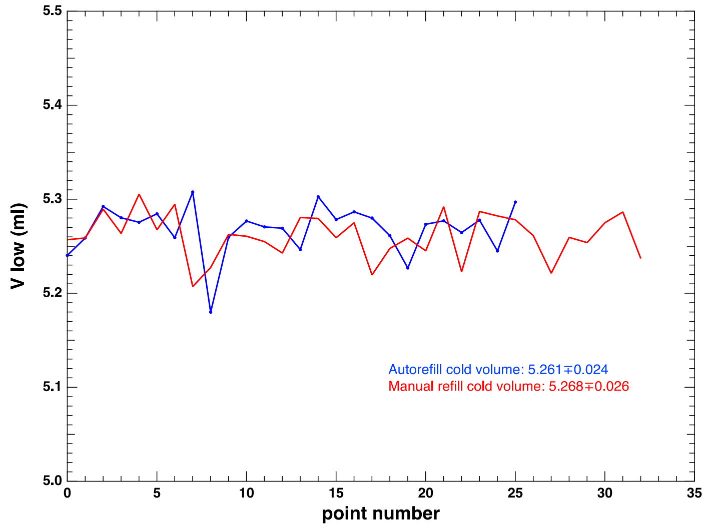
Accomplishment: Automated LN2 Refill







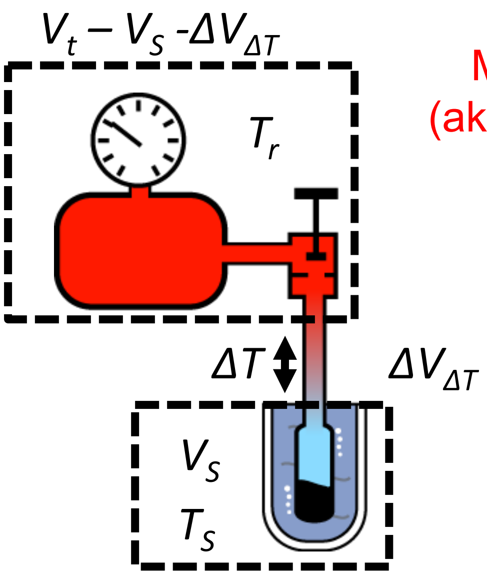
Verified operation of LN2 autofill apparatus to produce accurate and reliable measurements:

- Automated refill has significantly improved pressure stability relative to manual refill (empty sample tube).
- Calculated cold volume using autofill and manual fill are consistent (empty sample tube).
- Gravimetric capacity (wt%) at 77K is consistent with multi-laboratory study results

Relevance/Approach: Measurement Validation & Error Analysis

Relevance:

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

Approach:

- **Assist materials-research groups**
  - Validate external samples at NREL
  - Discover sources of discrepancies
  - Advise on corrective actions
- **Investigate sources of measurement error**
  - Analyze realistic models
  - Identify major error sources
  - Recommend improvements
    - Instrumentation
    - Experimental procedures
    - Data analysis
- **Disseminate Findings**

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Accomplishments: Measurement Validation 2018

- **Milestone: Worked with groups funded by DOE to validate measurements and analyze results.**
  - 2 Validated sample capacities. Results reported to DOE.
    (Data is considered proprietary and cannot be shared.)
    (Measurements include TPD, PCT, BET etc.)
    41 measurements
  - Trained new post doc for PCT measurements

- **Collaborated with groups for sample measurements, discussion of error analysis and advisement on protocols to enhance accurate measurements.**
  - 4 groups (Berkeley, University of Delaware, Sandia (HyMARC), Ford)
  - Collaborated with HYMARC – measured 2 samples - 17 measurements

FY18 Characterization Milestones

Description	Due	Status
9. Construct a cryo-autofill apparatus for the second PCT Volumetric PCTPro Instrument and evaluate samples at 77K (LN) for the routine determination of excess, total volumetric and gravimetric capacities	12/31/17	100% complete
10. Validate the variable-temperature PCT apparatus performance, stability and appropriate void sample holder parameters at 5 discrete temperatures that span 77 K to 323 K.	03/31/18	100% complete
11. Determine the isosteric heats of appropriate Framework/Sorbent material from the materials section of this AOP with the variable-temperature PCT apparatus at the 5 discrete temperatures that span 77 K to 323 K.	06/30/18	In progress; slightly behind schedule.
12. Measure and validate the gravimetric capacity, volumetric capacity of 2 samples as assigned by DOE. Submit full report to DOE within 30 days of completion of analysis.	09/30/18	In progress and on schedule. 1st sample already measured and reported on. 2nd sample awaiting DOE request.

Future Work & Challenges

- **Volumetric Capacity: Inter-Laboratory Comparison**
  - Finalize editing and submit ILC18 manuscript to journal.
  - Develop 2nd manuscript with more detailed analysis.
- **Thermal Conductivity Measurement and Validation**
  - Finish validation work; provide routine measurements
  - Publish MOF5 results
- **Variable-Temperature PCT**
  - Verify operation of cryostat with existing PCT instrument to produce accurate and reliable measurements
  - Integrate new hardware and LabVIEW software into instrument
  - Validate isosteric heat of adsorption measurement
- **Measurement Validation & Error Analysis**
  - Need to validate 1 more sample (FY18)

Any proposed future work is subject to change based on funding levels

Summary

- **Volumetric Capacity: Inter-Laboratory Comparison**
  - Inter-laboratory comparison is complete.
  - First manuscript submission immanent.
- **Thermal Conductivity Measurement and Validation**
  - Validation studies are complete.
  - Thermal conductivity measurement for others on-going.
  - Instrumentation publication planned for near future.
- **Variable-Temperature PCT**
  - Hardware integration is complete.
  - Additional validation testing on-going, followed by sample measurements.
- **Measurement Validation & Error Analysis**
  - More samples are expected for validation.
  - Error analysis and assisting others is continuing.

Acknowledgements

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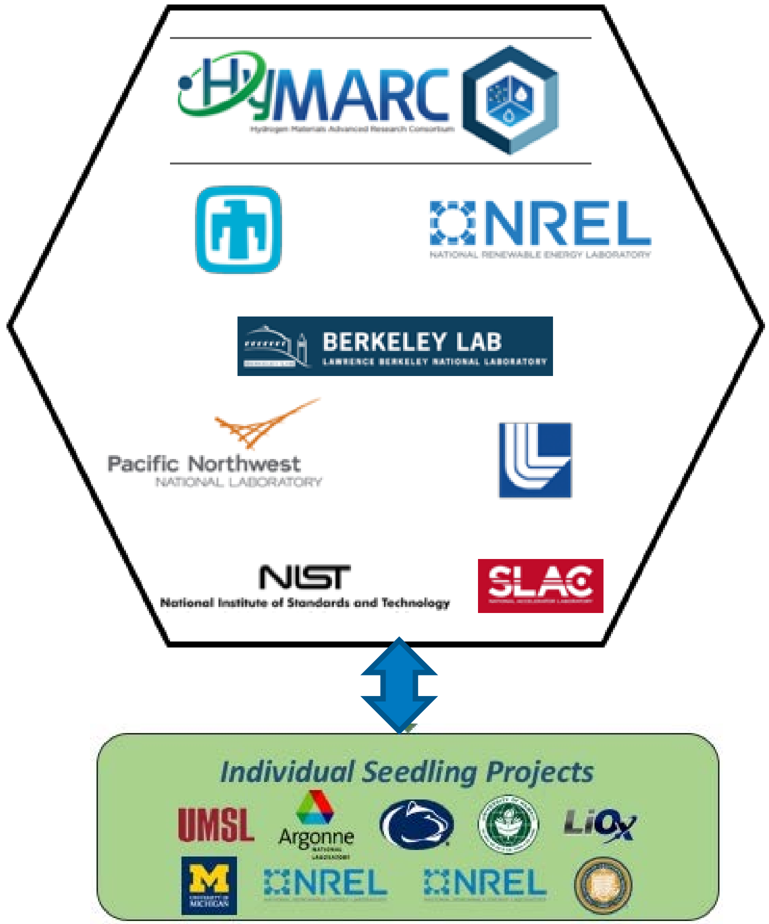

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Technical Back-Up Slides

Inter-laboratory Measurement Study - Samples

Two Carbon Samples:

- **Sample 1:**
  - Norit ROW
  - Pellets
  - BET SSA 740 m^2/g
- **Sample 2:**
  - MSC20
  - Powder
  - BET SSA 2400 m^2/g

Inter-laboratory Measurement Study - Run Sheet

Participants were asked to fill out a *Run Sheet* that included experimental information.

<u>This included:</u>

- **sample mass (before/after degas)**
- **skeletal density**
- **packing density**
- **methods for determining skeletal density**
- **hydrogen purity**
- **equation of state**
- **whether degas protocol was followed**
- base pressure for degas instrument
- base pressure for volumetric instrument
- equilibrium time for adsorption
- temperature stability
- pressure sensor accuracy

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INTER-LABORATORY COMPARISON RUN SHEET

INSTRUCTIONS

Please fill out a run sheet for each measurement. You may want to fill out the fields that will be common for all measurements and then save this file so you do not have to fill in those fields every time.

Please provide isotherm data calculated as excess gravimetric (wt%), excess volumetric (g H_2/L) and total volumetric (g H_2/L) in either tab-delimited format or an Excel spreadsheet. See the instruction sheet for additional details. If you correct for helium adsorption that occurs during the calibration, please supply both the corrected and uncorrected data if possible.

If you have any questions call or email Katherine Hurst (303-384-7673; katherine.hurst@nrel.gov)

LABORATORY INFORMATION

Laboratory Institution | **Person filling out run sheet**

Phone number for person | **E-mail for person**

Filename(s) for this data:

NOTE: The above information will be removed when the final results are reported. Laboratories will be identified anonymously using a randomly assigned number.

SAMPLE TYPE: ☐ Sample 1 or ☐ Sample 2

SAMPLE PREPARATION (skip if null measurement data)

SAMPLE MASS

Initial Mass: ± mg Date:

After degas (optional): ± mg Date:

Final Mass: ± mg Date:

SAMPLE DEGAS **Begin Date:** **End Date:**

Base Vacuum Pressure: Units:

Degas Protocol: ☐ **Degas protocol followed** ☐ **Degas protocol exception (explain)**

Degas Explanation:

Was sample exposed to air after degas and prior to measurement? ☐ **No** ☐ **Yes (explain)**

Air Exposure Explanation:

MEASUREMENT INFORMATION

Measurement Method: ☐ **Gravimetric** ☐ **Volumetric** ☐ **Other:** | ☐ **Static** ☐ **Dynamic**

Measurement Temperature: ☐ **Liquid Nitrogen** ☐ **Ambient:** **K** | **If dynamic, flow rate:**

Hydrogen Purity: **%** **Additional purifier used?** ☐**Yes** ☐**No**

Base Vacuum Pressure: Units:

Sequence order: ☐ **He calibration done first** ☐ **H_2 measurement done first**

Equilibrium time/step: (min.) | **Total time for measurement:** min.

Temperature stability: **Standard Deviation:** **K** | **Pressure Sensor Accuracy:** **%** ☐ **FS** ☐**Reading**

Equation of State: ☐ **Ideal** ☐ **Real:** **Model:**

CALIBRATION

Helium adsorption correction: **Supplied data has** **Method:** no correction **if other, explain:**

Skeletal Density: ☐ **Not Measured** ☐ **Measured:** **g/cm^3** **Method used:**

Packing Density: **Measured:** **g/cm^3** **Method used:**

COMMENTS

2/15/16

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Definitions for Inter-Laboratory Metrics

- **Gravimetric Excess Capacity**

$$wt.\% = \frac{100\, m_{ex\,H}}{m_s + m_{ex\,H}}; \quad m_{ex\,H} = M_{H_2\,AMU}\, n_{ex\,H_2}$$

- **Volumetric Excess Capacity** (normalized by packing volume)

$$\Lambda_{ep} = \frac{m_{ex\,H}}{V_{pk}}$$

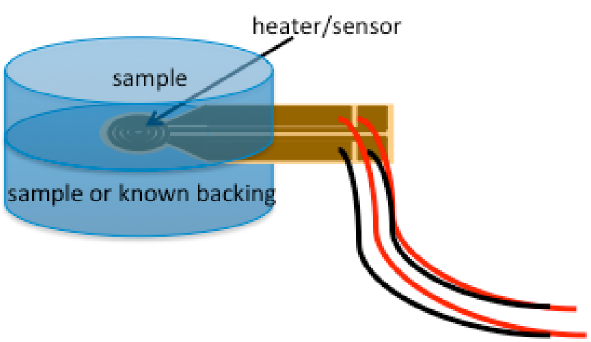
- **Volumetric Total Capacity** (normalized by packing volume)

$$\Lambda_{tp} = \frac{m_{tot\,H}}{V_{pk}} \qquad n_{tot\,H_2} = n_{ex\,H_2} + \rho_{fg}\left(V_{pk} - V_{sk}\right)$$

Thermal Conductivity Apparatus

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

- ***Transient Plane Source Technique***
- 40 K to 375 K
- up to 100 bar
- capable of measuring pucks and powders (down to ~ 1 cm^3)



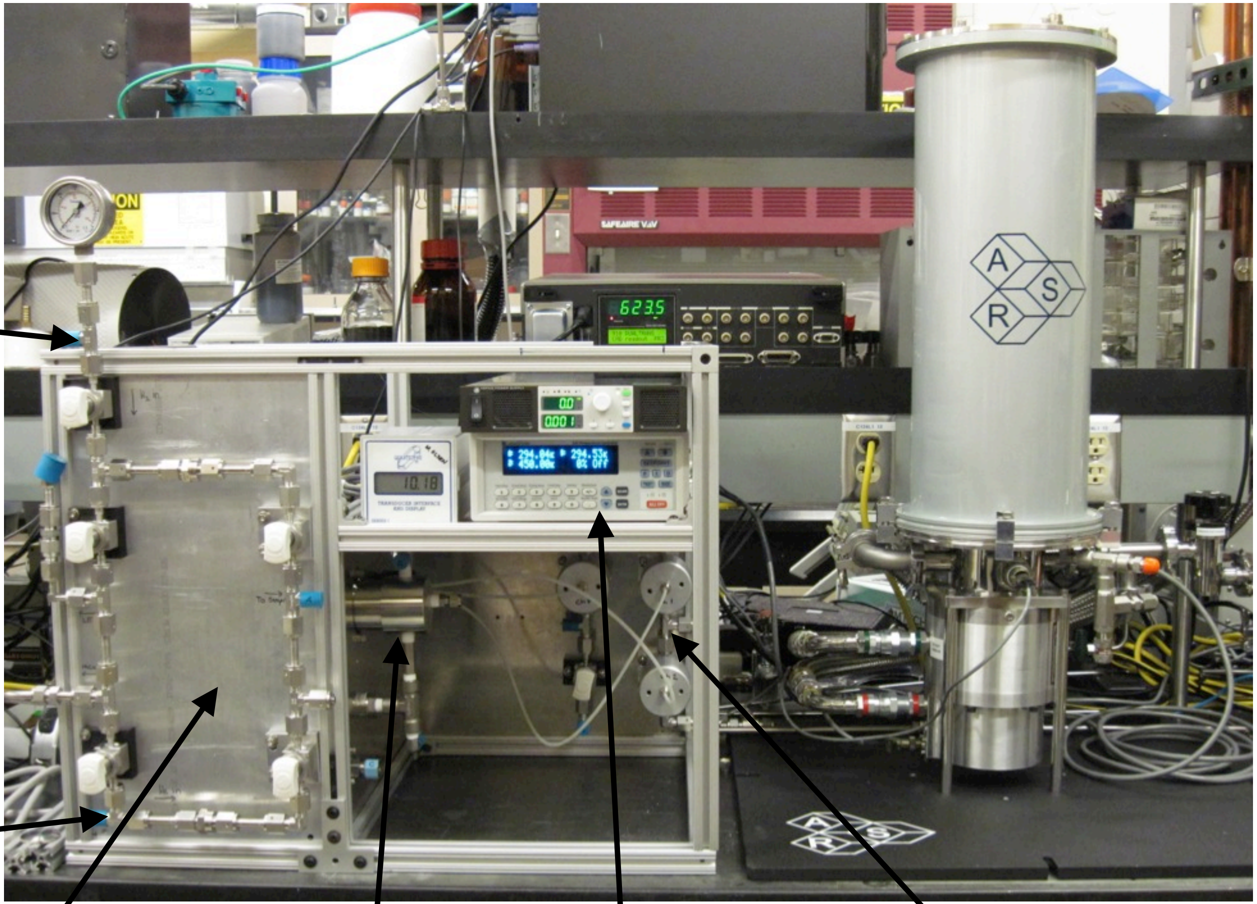
Thermal Conductivity: Cryostat and Pressure-Control System

System was built in FY16

Hydrogen inlet

(Control electronics behind manual valve panel)

Helium inlet



Manual valves

Pressure regulator

Cryostat temp. controls

Pneumatic valves