HySCORE: NREL Technical Activities

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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

ST131

Overview

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

NREL:
FY17 = $1.44M
FY 18 = $1.0M
Total = $3.625M

Note: FY18 includes $250k for data management

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 – Core Team – 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

Relevance: HySCORE Objectives

Collaboration and synergistic research effort

Enabling twice the energy density for onboard H_2 storage

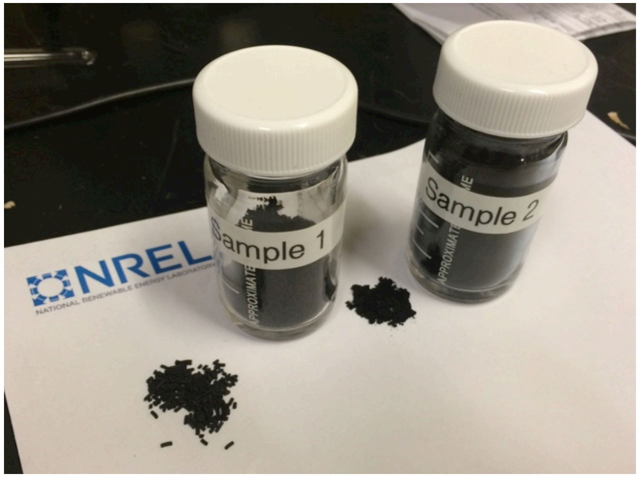
- **To *Develop* and *Enhance* Hydrogen Storage Core Capabilities, i.e. Characterization Techniques**
  - NMR, DRIFTS, PCT, TC, TPD, Calorimetry, Neutron. X-Ray
- **To *Validate* claims, concepts and theories of hydrogen storage materials**
  - Properties of gas-solid interactions in high surface area materials
  - Benchmarking theory
- **To *Accelerate* the path forward to development of hydrogen storage materials for transportation**
  - Provide insight into the kinetic and thermodynamic bottlenecks
    - Rational design of new materials
    - Unravel complex phenomena

Tom Gennett, Phil Parilla **Jeff Long, Martin Head-Gordon,** **Tom Autrey, Mark Bowden,** **Craig Brown Terry Udovic**

Relevance: 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**

Accomplishment: ILC Data Analysis

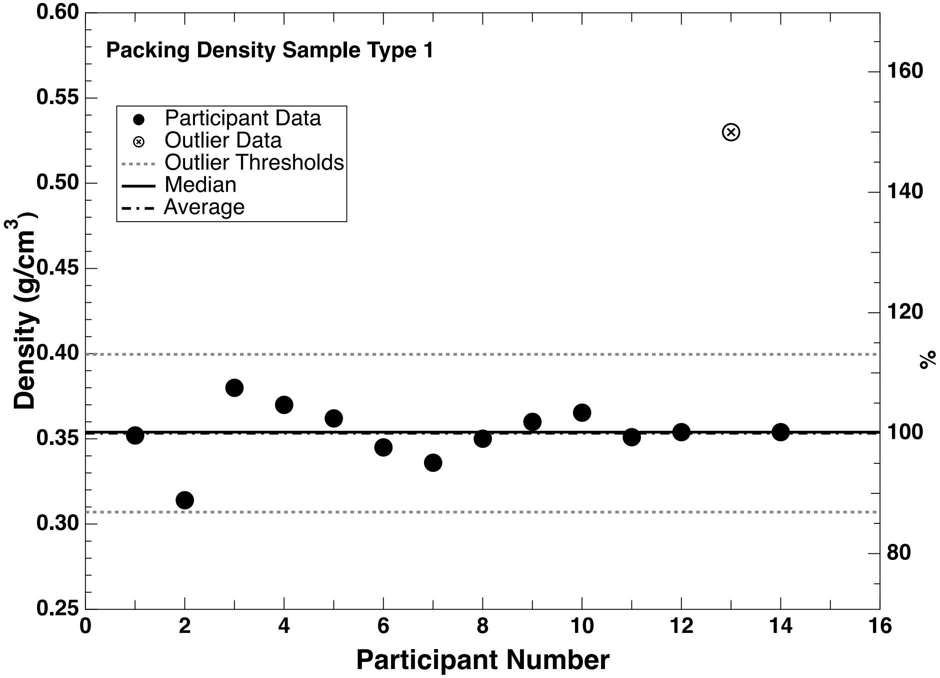


- **Data Received:**
  - 14 data sets at ambient conditions Sample 1
  - 13 data sets at ambient conditions Sample 2
  - 10 data sets at liquid N_2 data Sample 1
  - 9 data sets at liquid N_2 data Sample 2

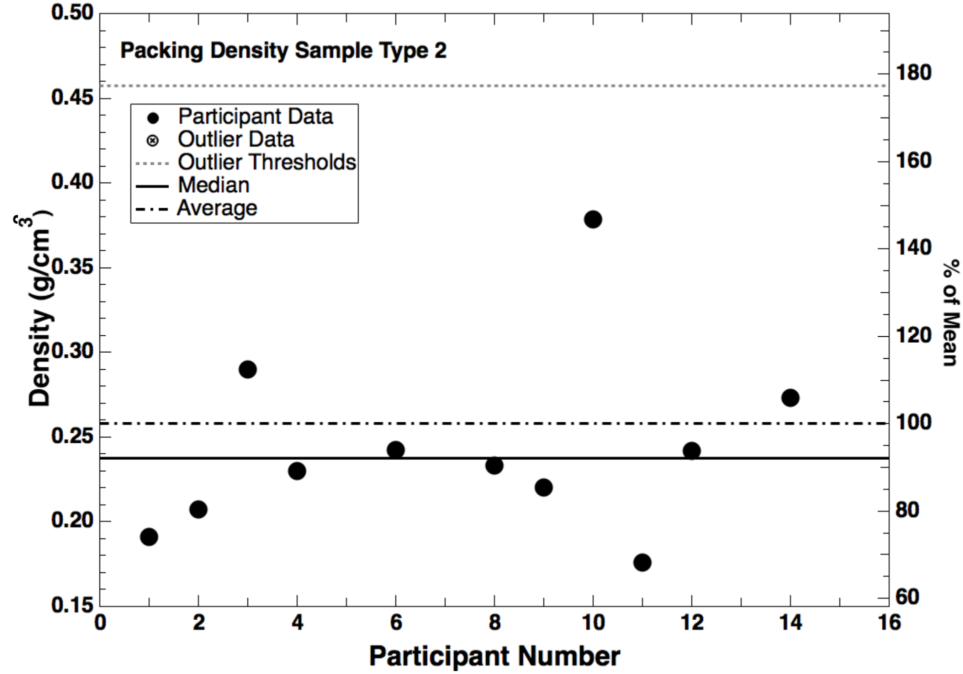
- **Data Analysis:**
  - Data received was inspected and investigated for gross errors
  - Isotherms were interpolated to a common set of pressures to allow statistical analysis
  - General analysis is completed.

Progress: Packing Densities Impacted Volumetric Capacities

Sample Type 1

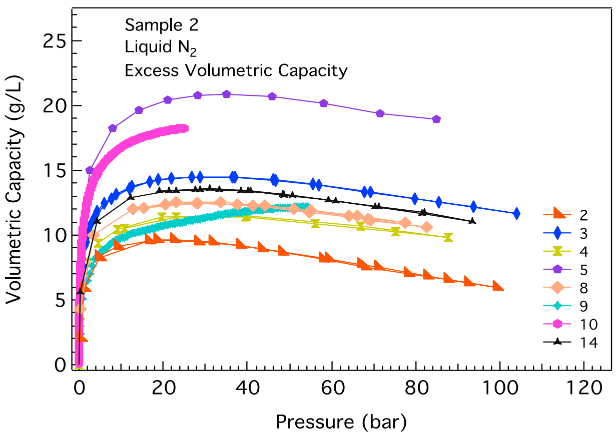


Sample Type 2



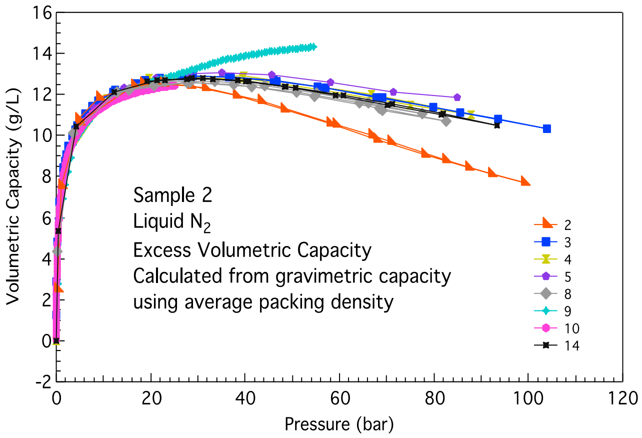
- Powder sample, Sample 2, has a much higher variability in packing density than pelletized material, Sample 1.
- One outlier for volumetric capacities
- **The variation in packing density directly affects the total and excess volumetric capacities**

Accomplishment: Importance of Packing Density

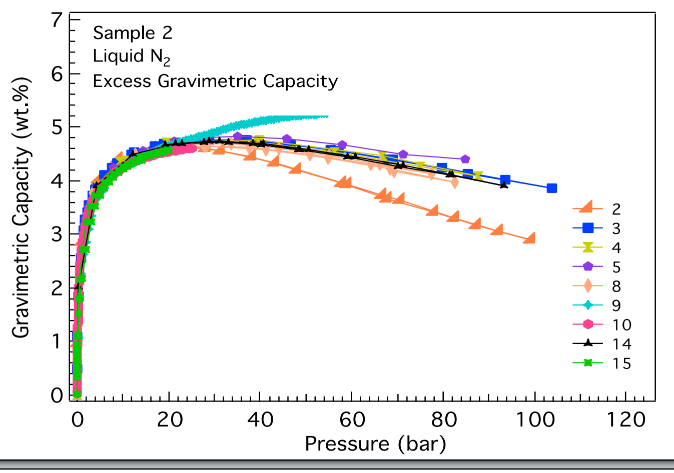


Note change in y-axis scale

Re-normalizing to study's average packing density



The variability now similar to gravimetric excess measurement



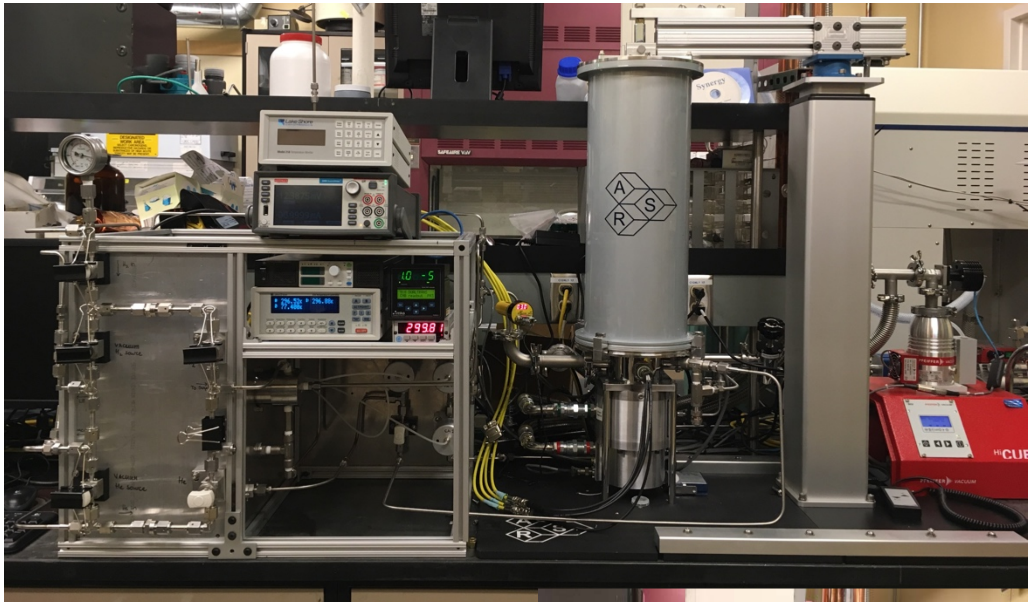
- **THIS EMPHASIZES THE IMPORTANCE OF HOW THE PACKING DENSITY IS DETERMINED**
- **Manuscript completed**

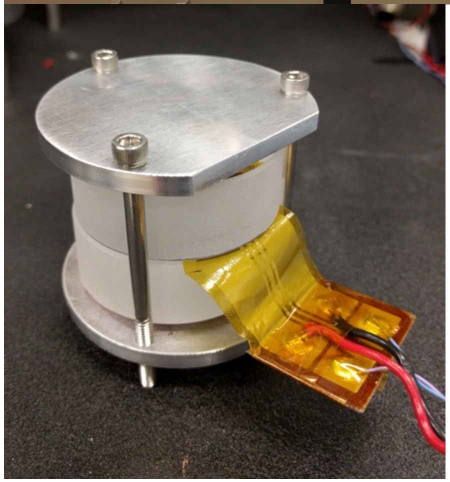
Accomplishment: Thermal Conductivity Apparatus

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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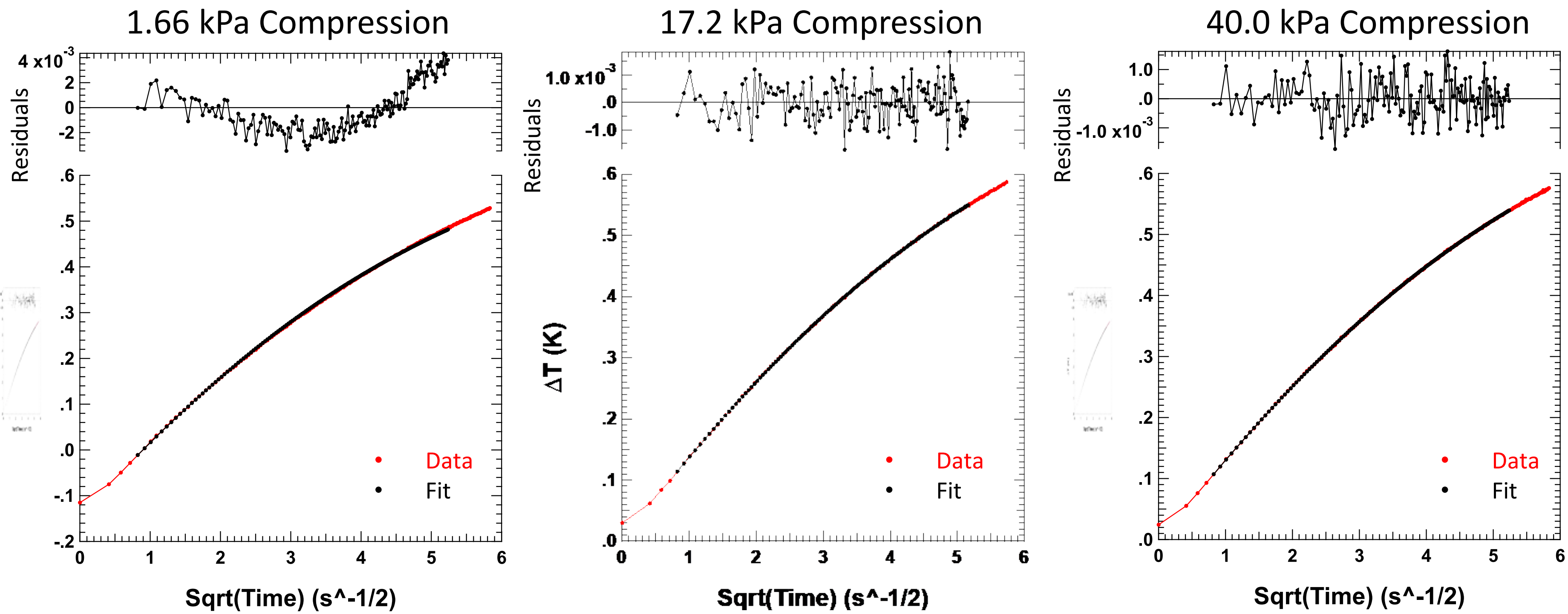
Accomplishment: TC – Steel Powder Validation



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

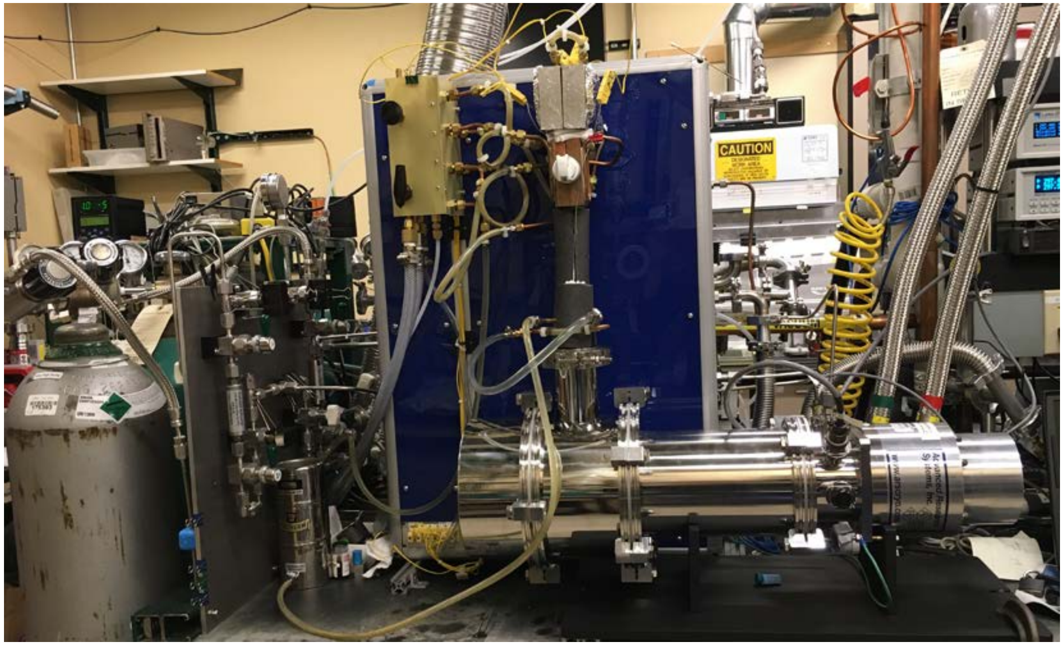
* Temperature calibrations are preliminary

Progress: 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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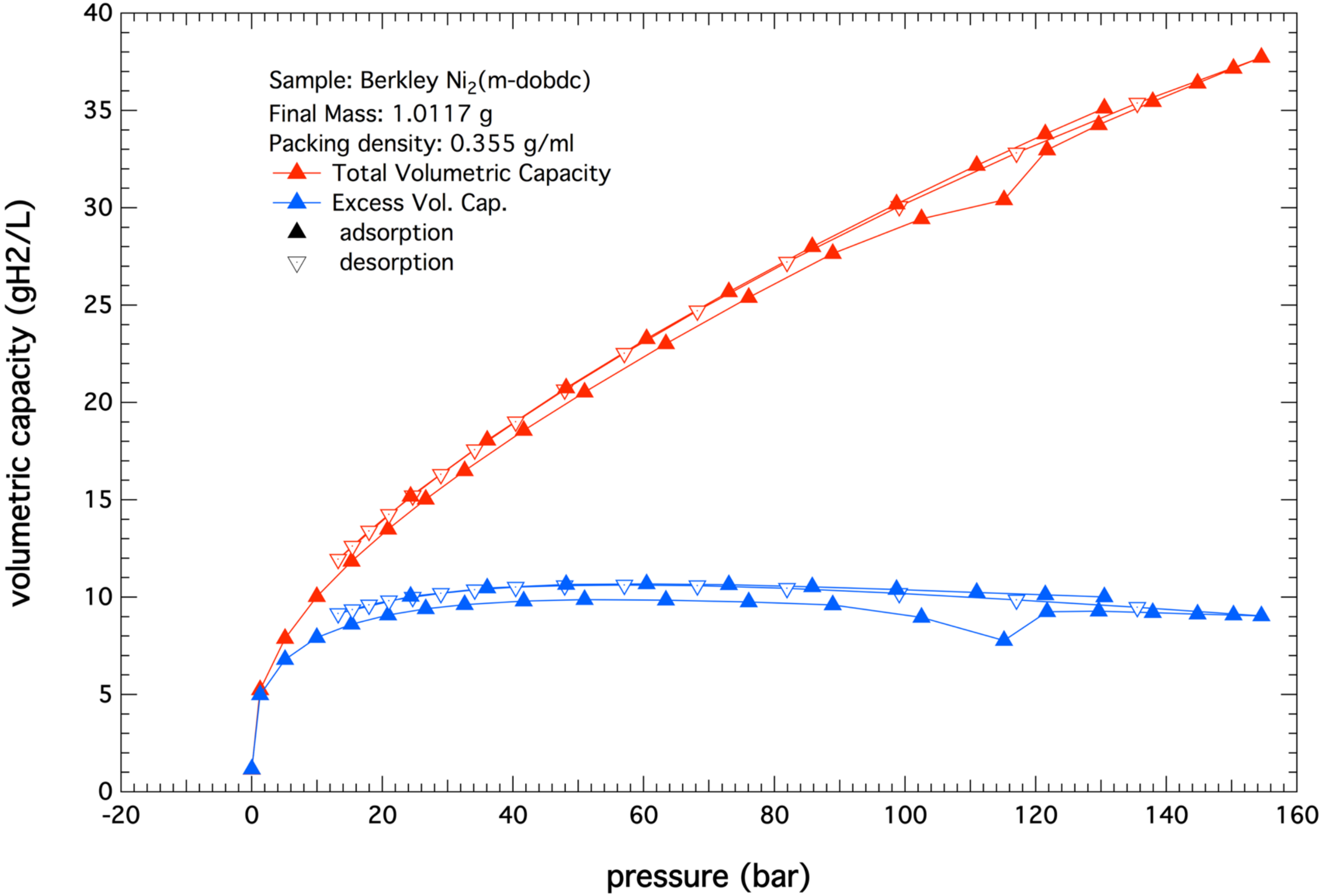
Accomplishment: LBNL Sample Measured at 100 K

Volumetric Capacity



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 - 17 measurements

Collaboration: Support of seedling projects

Project: *Fluorinated Covalent Organic Frameworks: A Novel Pathway to Enhance Hydrogen Sorption and Control Isosteric Heats of Adsorption (NREL)*
Purpose: Characterize structure (TEM), stability (TGA), SSA and pore size of COF series, and H_2 uptake (TPD), SAXS analysis at SLAC

Project: *Univ. of Hawaii Seedling*
Purpose: Confirm U. Hawaii H_2 wt% measurements using TPD and TGA

- Analyzed 2 materials
  - MgB_2 + Mg + THF
  - $MgB_2 + MgH_2$

Project: *Atomic Layer Deposition (ALD) Synthesis of Novel Nanostructured Metal Borohydrides (NREL)*
Purpose: Assist with TPD measurements to determine effect of Al_2O_3 ALD coating on H_2 desorption peak of $Mg(BH_4)_2$, SLAC Characterization

- Characterization using AP-XPS at SLAC
- Preliminary cyclability test of H_2 capacity using PCT and TPD on ALD coated $Mg(BH_4)_2$

Project: *ANL Graphene coated $NaBH_4$*
Purpose: TPD experiments to evaluate samples for desorption processes and outgas composition

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.
- **Seedling Project Support**
  - PCT, TPD, DTA/TGA, SAXS, TEM, XRD, BET analyses

Future Work & Challenges

Subject to change based on funding levels

- **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)
- **Characterization**
  - Expand to the new capabilities available at SLAC
    - Design and validate new sample cells

Relevance: Mass Transport Control of Hydrogen Sorption

Can we achieve kinetic control of desorption through manipulation of pores?

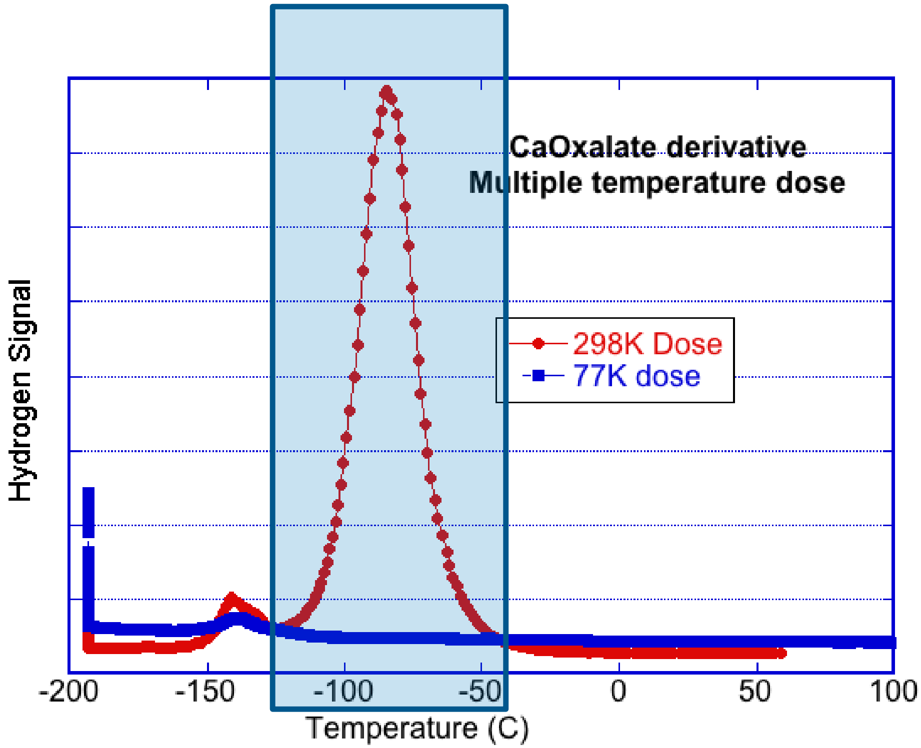
- **N_2 BET surface area are very low**
  - Pores are smaller than the kinetic diameter of nitrogen (3.6 angstroms) while hydrogen (2.9 angstroms) can still enter the framework
  - Minimize structural changes with temperature
- **Kinetic vs thermodynamic vs “disorder” effect**
  - Binding energy vs. “diffusion” limits
  - Size exclusion
- **Hydrogen Dose Temperature and Pressure**
  - Control kinetics of desorption and adsorption
- **Vibrational Phonon Effect?**
  - Will this allow control the desorption temperature?
  - Isosteric heat control

Approach: Small Pore Materials (<1nm) HySCORE

Large Hydrogen Desorption peak at approximately 180 K, approx. 1.2% Hydrogen at 100 bar and 190 K

Unusual Behavior of Calcium Oxalate

- **BET measure surface area 4 m^2/g**
- **No hydrogen adsorbed if dosed below 150K**
- **First small pore material with apparent phonon sorption limitation above 50K**

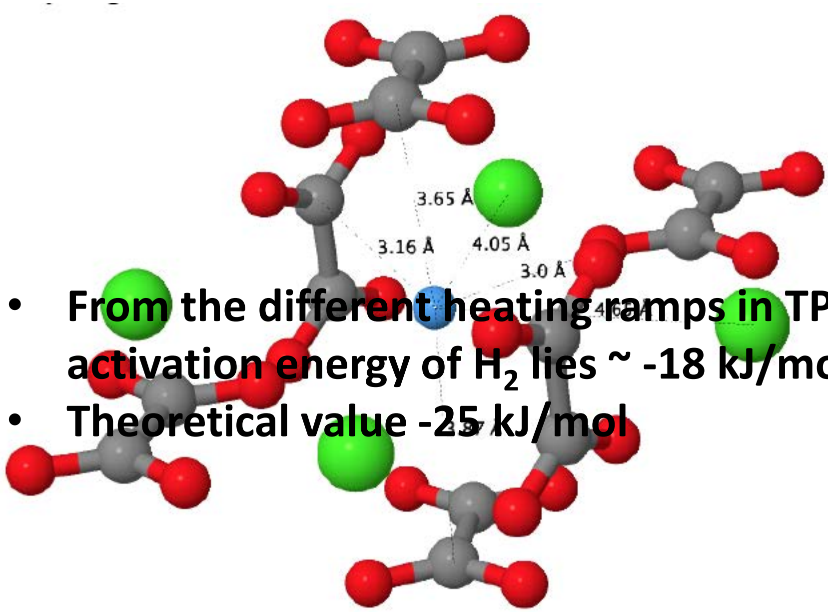


Converts to dehydrate at 180 ˚C with no intermediate (Mark Bowden, PNNL)

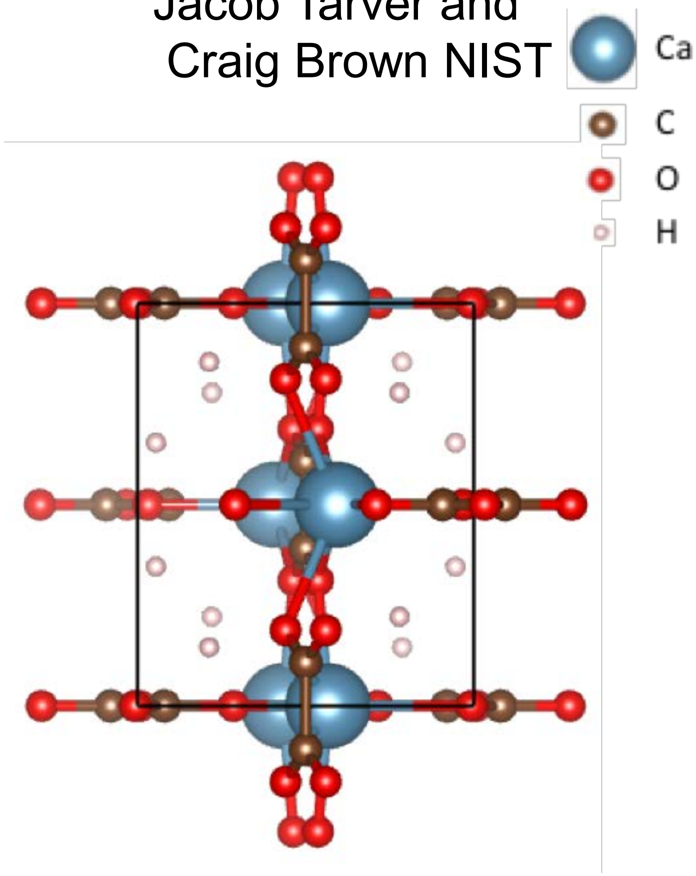
Accomplishment: Hydrogen bonding sites in Calcium Oxalate, DFT and Experimental

Density Functional Theory (DFT) calculations. Martin Head-Gordon LBNL

Jacob Tarver and Craig Brown NIST



- **From the different heating ramps in TPD, the activation energy of H_2 lies ~ -18 kJ/mol**
- **Theoretical value -25 kJ/mol**



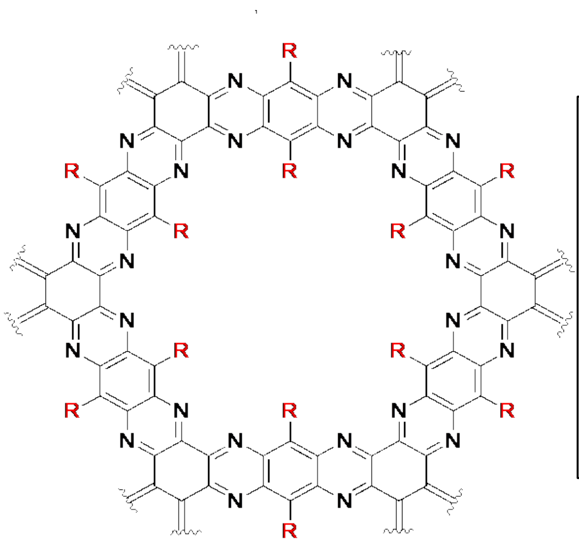
A picture showing the nearest neighbors of hydrogen.
Green – Ca, Red – O, Gray – C, Blue H
Approx. 4 angstrom pore size

Approximate position of Hydrogen is near the oxalate small pores, not the calcium

Approach: 2-D C_2N Framework Materials

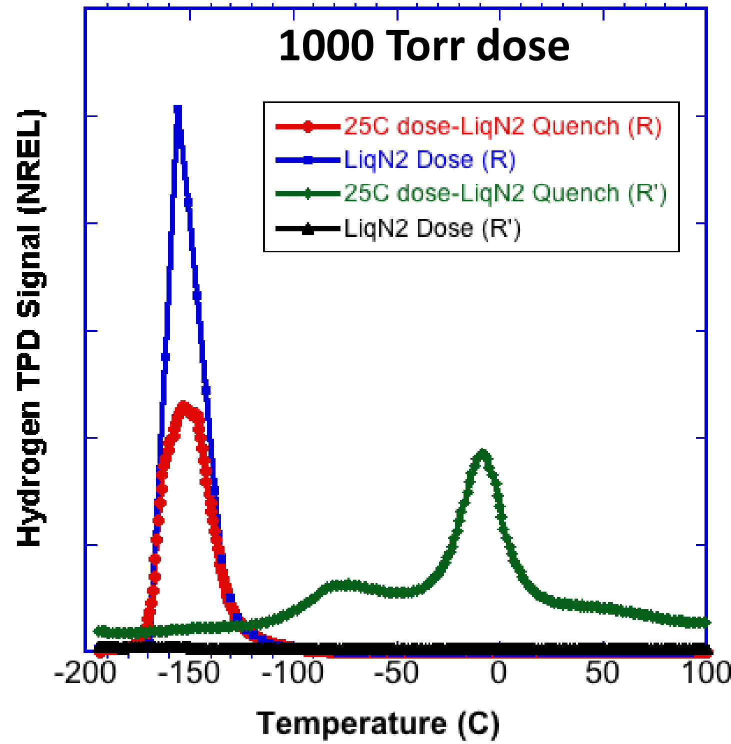
Characterize initial H_2 sorption properties with TPD and PCT,
Compare results from different synthetic routes and R groups (see structure)

- **Measured multiple samples with varying R groups and synthesis methods with TPD**
  - **R = CO_2H**
  - **Physisorption slower at lower temperature**
  - **Desorption peak at 0˚C**
  - **PCT at 77 K confirms slower adsorption kinetics**



R = H – 100%
R' = COOH - 100%

For R'
BET – 22 m²/g (185 m²/g – CO_2)
Pore size 3.5 - 20 angstroms



Univ. Wyoming – Bruce Parkinson

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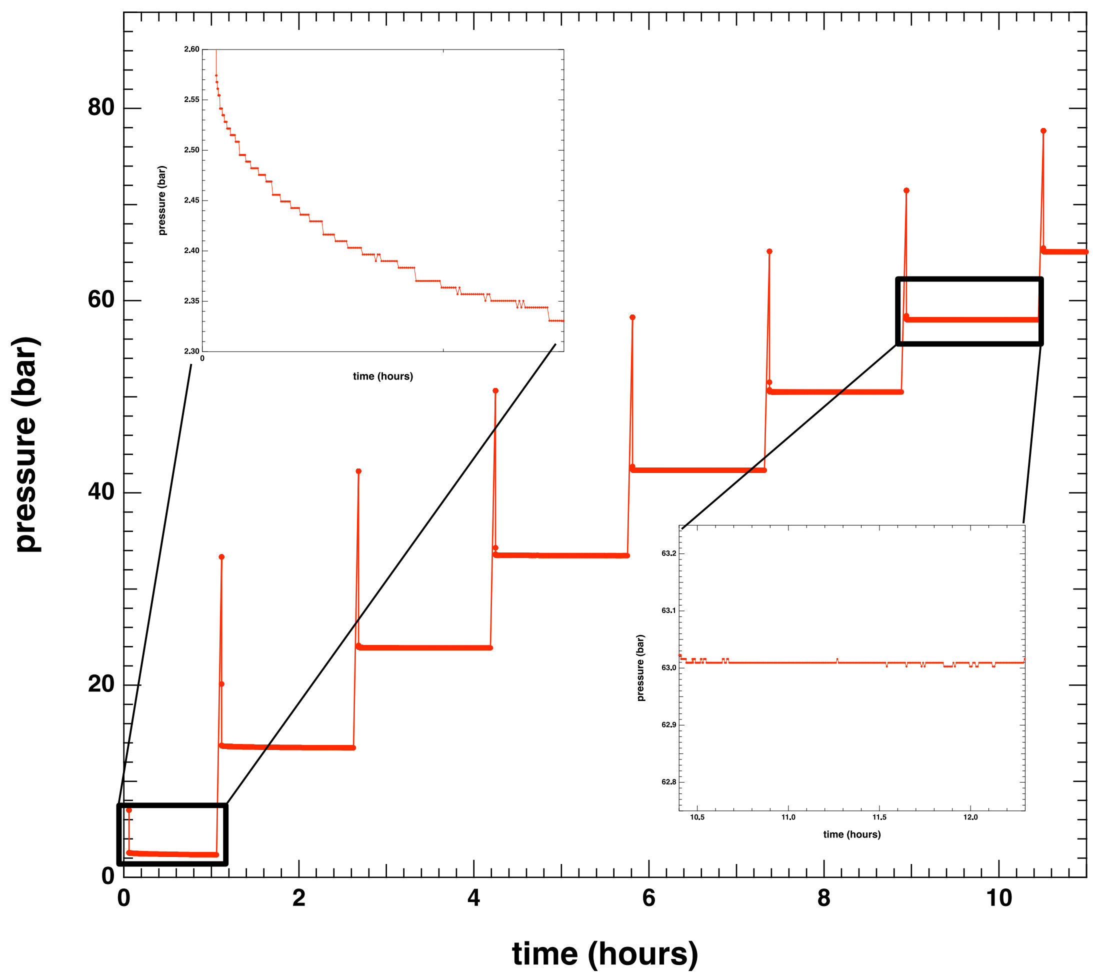
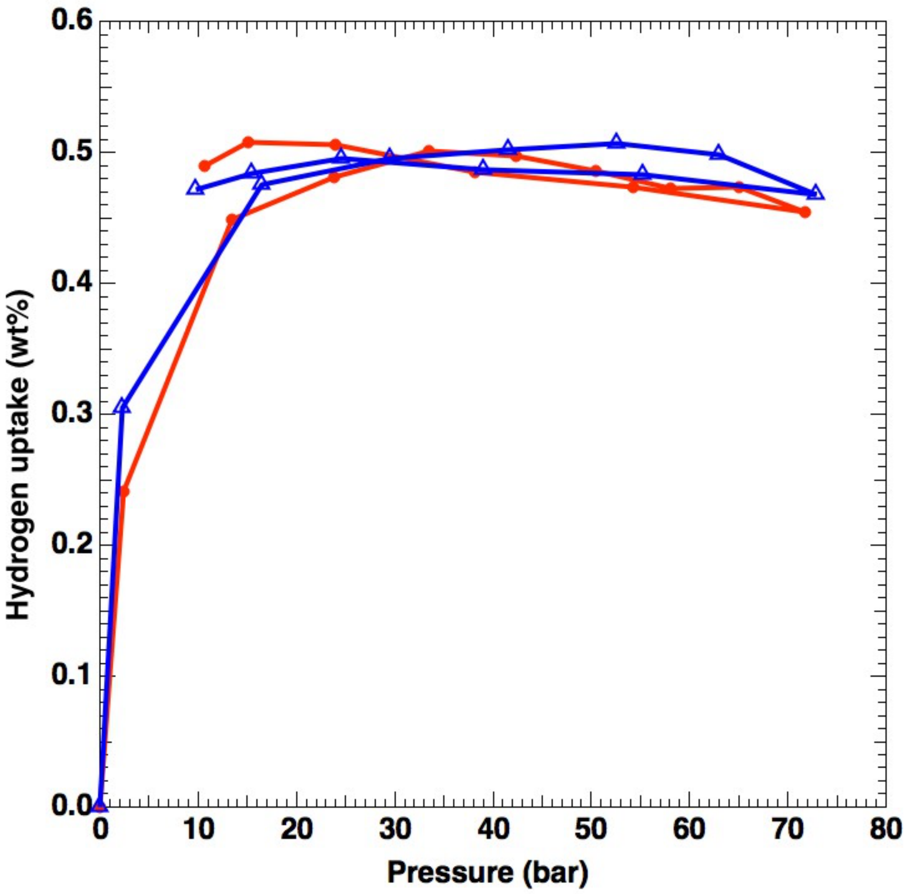
Accomplishment: PCT 2-D C_2N materials 77K

- **Long Transient, at low pressure**
  - **No Chemical Reactions**
  - **Kinetic limitation**

- **Equilibration time decreased with increasing pressure.**

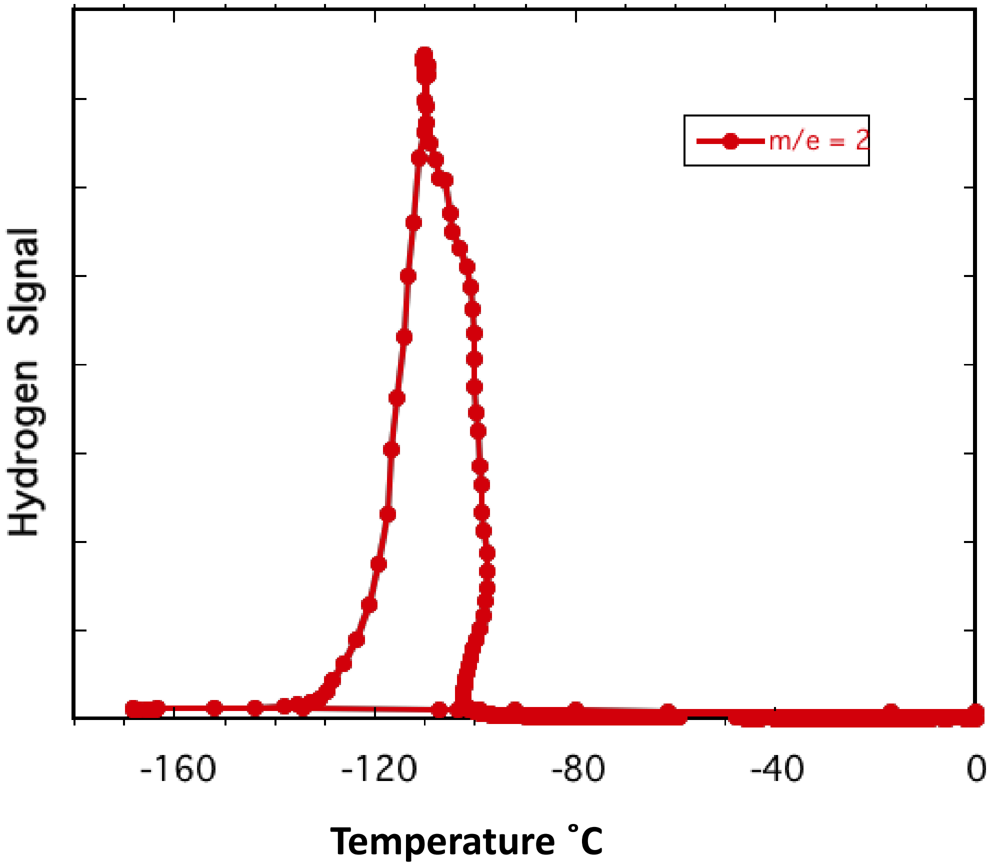


Accomplishment: C_2N Material, Desorption



- On reverse desorption cycle, Hydrogen did not come off the sample. i.e. a large Hysteresis (red)
- H_2 was removed with high vacuum at 77K and the PCT run was repeated (not shown). Started from hysteresis point
- H_2 was removed with vacuum at room temperature and the PCT run was repeated – the hysteresis effect re-occurred aligned with the initial data.

Accomplishment: Increased Desorption Temperature



- Unlike CaC_2O_4, Hydrogen will adsorb at 77K with high pressure.
- Hydrogen is not released until system at ~ 163K (-110 ˚C)
- Amount of Hydrogen recovered via mole counting, removed all hysteresis
- Mass Transport
- Need to evaluate release with H_2 backpressure

Future Work: subject to change based on funding levels

C2N Materials

- High pressure single dose to determine barrier to adsorption
- Manipulate the R groups to optimize desorption temperature
- Optimize surface area for enhanced capacity levels
- Determine deliverable hydrogen in appropriate pressure ranges.
- Introduce possible additional binding sites to improve capacity

BCx Materials

- Complete position paper

Data Management (reviewer only slides)

- EMN requirement

Hydrogen Carriers (New H2@SCALE)

- Technoeconomic analysis, materials sets, forecourt/delivery requirements, solids, liquids.

Summary: Materials

Determined the ability to release hydrogen through control of thermal phonon vibrational mode for Calcium Oxalate

Established that in very small pore size materials it is possible to control hydrogen adsorption and desorption properties through possible mass transport limitations

Established that limitations of catechol functionalization of pyrolyzed PEEK sorbent materials does not allow for increased hydrogen storage capacity, but does increase binding energies.

Heterogeneously boron doped carbon materials to 4 atomic % B does not increase isosteric heats of adsorption for hydrogen. (Theory suggest an more ordered materials may be necessary)

Initial experiments on nitrogen doped carbon materials have begun to establish if nitrogen will increase isosteric heats of adsorption for hydrogen.

Major Goals

HySCORE

Near Term: (FY 18 milestone/deliverable driven)

- **Advance Core Capabilities:**
  - Variable temperature PCT for isosteric heats; *in-situ* DRIFTS measurement
  - Submit article on the round-robin results for further acceptance of protocols
- **Advance Materials Performance**
  - Improve capacity of new C2N sorbents. Alter the R group to enhance binding energies to complement "kinetic effects)
  - Determine the viability of nitrogen doped and nitrogen functionalized materials for increased binding energy and capacities that could approach 2020 goal
- **Advance Systems Modeling**
  - Refine and enhance the current modeling efforts with constant theory-experiment interactions. We need to improve our communication with theorists
- **Advance the collaborations within the expanded HyMARC team**
  - Establish a more seamless process to exchange data and samples via the new data management node
- **Initiate the HyMARC efforts on analysis of hydrogen carrier materials**

Long Term:

- **Develop a hydrogen storage material delivered with a total materials based capacity of > 50 g/L above 150 K, but less than 353 K that is possible with hydrogen overpressures < 100 bar and reversible for multiple cycles.**

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 (Additional slides)	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.

Acknowledgements

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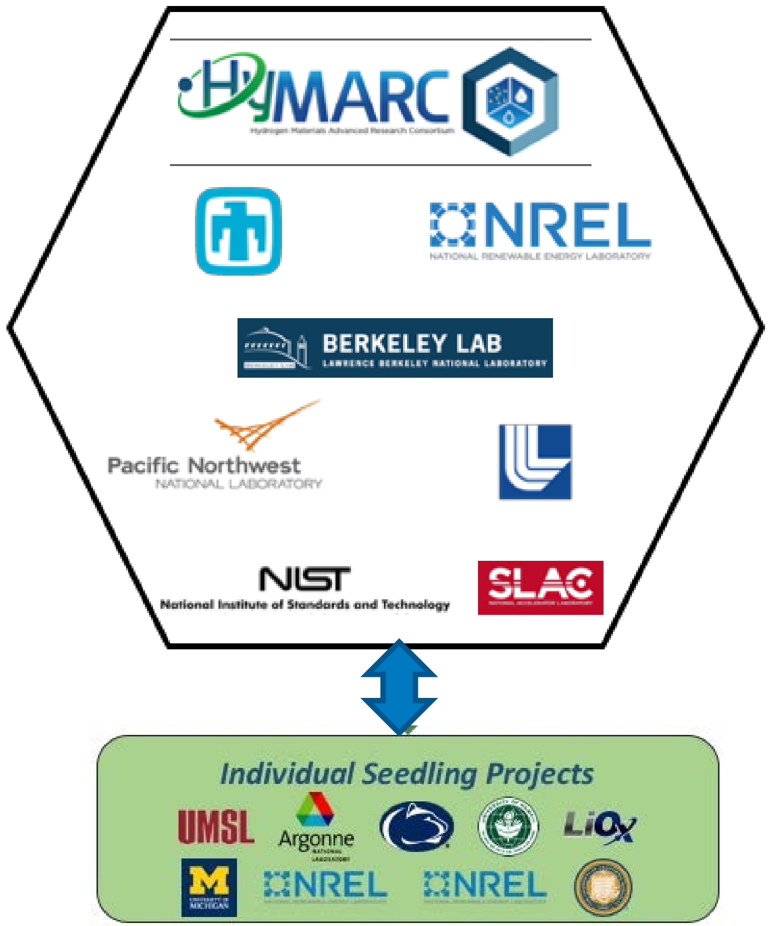

Technical back up slides

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2018 Annual Merit Review and Peer Evaluation Meeting

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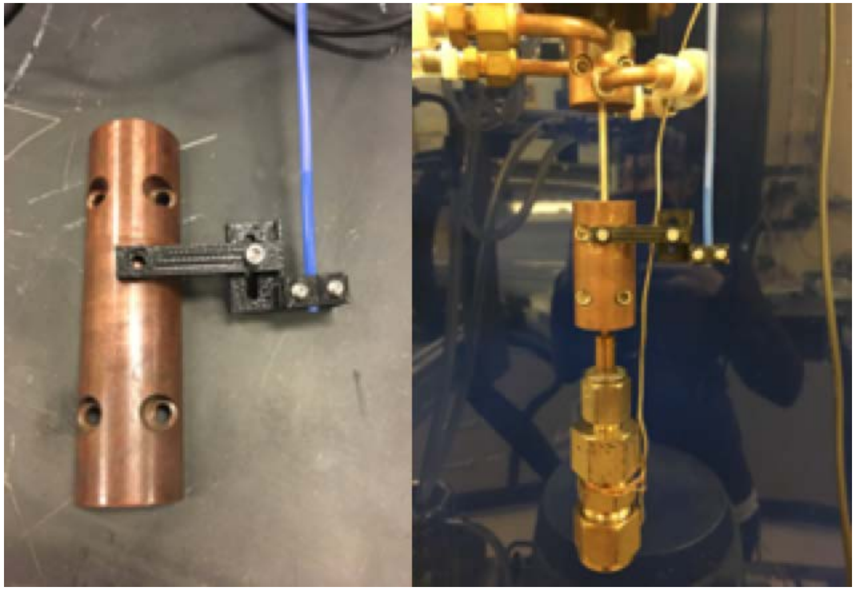
Accomplishment: Automated LN_2 Refill



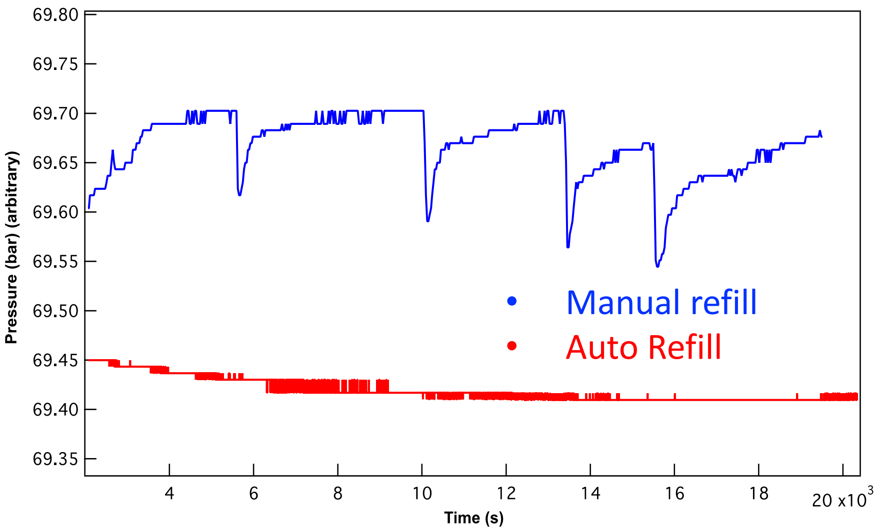
Autofill operation:

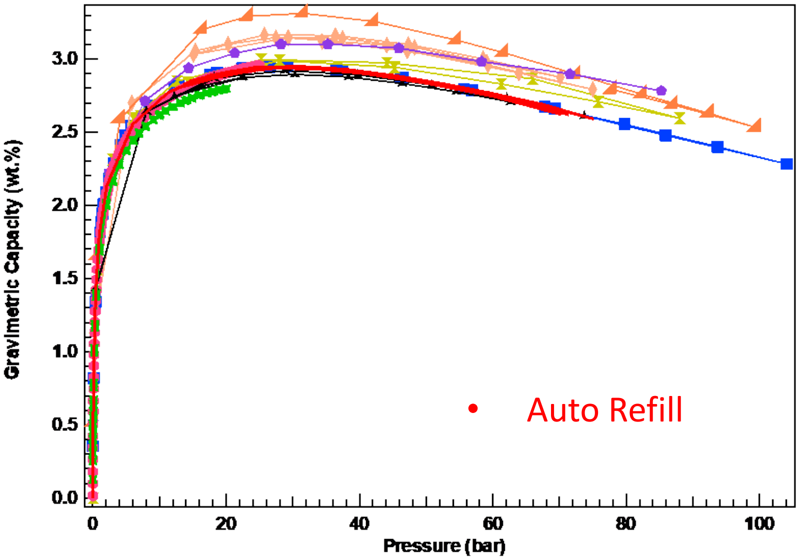
- Automated LN_2 refill apparatus utilizes a NORHOF #915 LN_2 Microdosing pump system.
- PT100 RTD sensor is inserted into the container at the desired level of the LN_2.

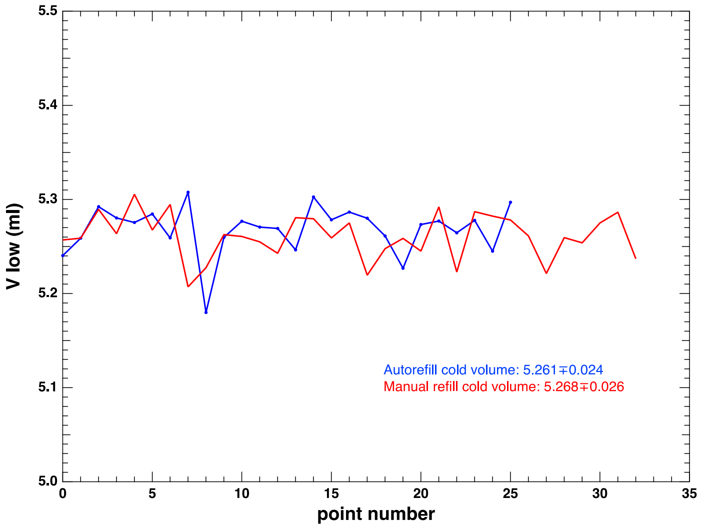
- Pump operates on a PID feedback loop with temperature feedback from the temperature sensor.

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

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

Accomplishment: Hydrogen Sorption, Calcium Oxalate

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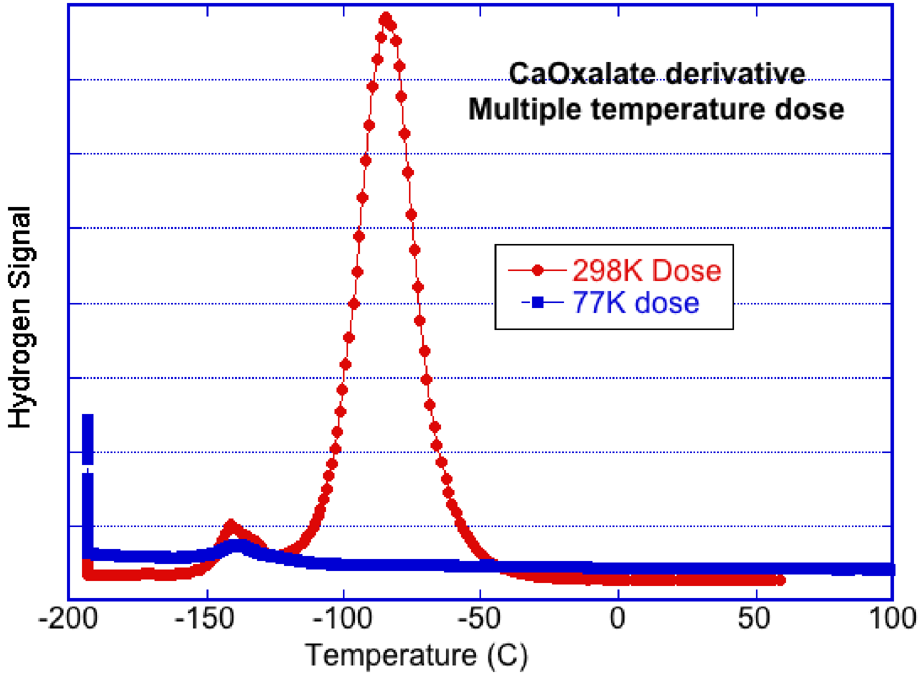

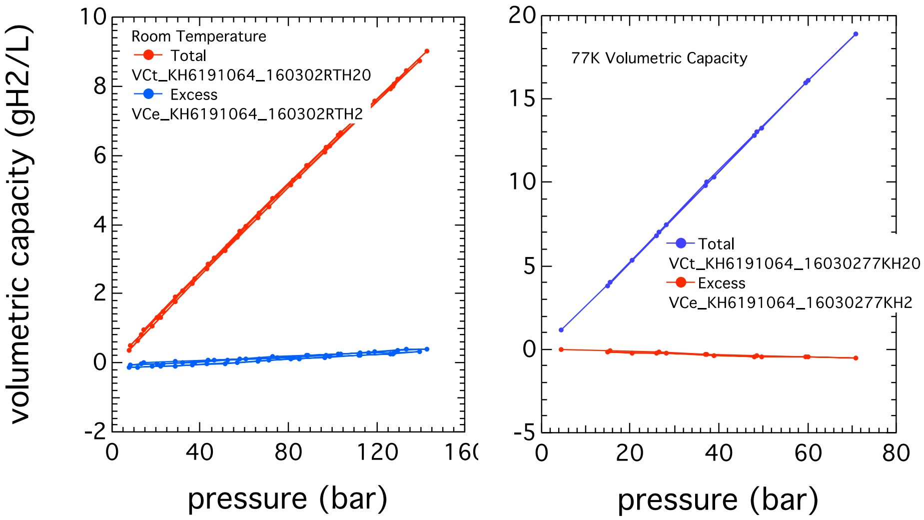

- PCT Room Temperature dose with 77K quench gives 0.75% w/w H_2
- **180K dose with 77K quench results in 1.2%w/w H_2 *<u>for a 4 m^2/g</u>* material**
  - **Mole counting experiment**
- At 77K there is zero adsorption after 6 hrs.