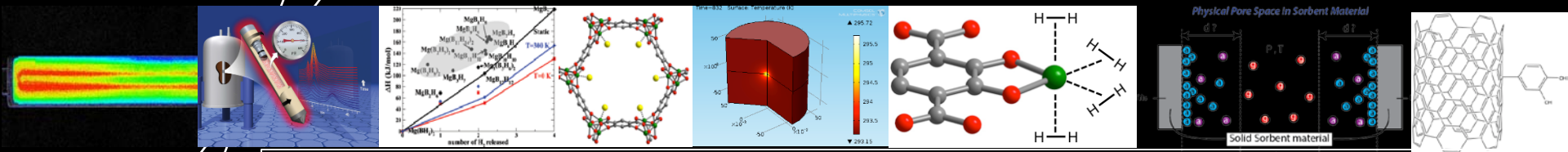
Project ID: ST131

# $H_2$ Storage Characterization and Optimization Research Effort




**DOE—EERE-FCTO Annual Merit Review**

**June 8, 2016**

**NREL Team: Rory Andrykowski, Jeff Blackburn, Arrelaine Dameron, Mira Dimitrievska (NIST), Suzanne Ferrere, Katie Hurst, Michele Olsen, Phil Parilla, Steve Robbins, Jacob Tarver (NIST), Jerry Tynan, Tom Gennett (PI)**

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

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

# Overview

## Timeline*

**Start:** October 2015
**End:** TBD
**% 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 FY16: $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 Chemi- sorption;
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 -** Troy Semelsberger
**H2Technology Consulting, USA -** Karl Gross
**$H_2ST^2$, USA -** Hydrogen Storage Tech Team
**IEA-HIA Task 32** - Michael Hirscher, Darren Broom

# Relevance

**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**

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

# Relevance

## Project Objectives:

**Develop new characterization capabilities.**

**- NMR, DRIFTS, PCT, TC, TPD, Calorimetry, Diffraction and Scattering**

**Validate "performance claims and theories" critical to the design of new hydrogen storage materials.**

## Impact:

**Access to advanced characterization and validation capabilities will accelerate research progress.**

**Rational design of new materials.**

- Unique opportunity to better understand the properties of gas-solid interactions in high surface area materials
- Provide insight into the kinetic and thermodynamic bottlenecks in complex hydrides and hybrid materials.

**Benchmarking theory.**

- Couple theory with experiment to benchmark and validate the computational predictions. (HyMARC collaboration).
- Unravel complex phenomena, guide experimental work and accelerate progress.

# Approach (All Partners)

NREL NATIONAL RENEWABLE ENERGY LABORATORY

ST131a and ST014

- Validation and characterization of sorbent physiochemical properties
  - Advanced PCT analysis
  - Thermal Conductivity (TC) with $T$ = 77-400 K, $P \leq$ 100 bar He/$H_2$
- Mechanistic validation:
  - can exposed cations in carbon-based sorbents reach target of $\Delta H = -15$ kJ/mol?
  - is it possible to control sorbent desorption temperature?
- Validate computational predictions of $H_2$ binding energies and capacities

Pacific Northwest NATIONAL LABORATORY

ST132

- NMR (i) solid state with precise $H_2$ dosing at $T$ = 10-300 K; (ii) in-situ MAS with $T$ to 400 K and $P \leq$ 200 bar (iii) variable pressure liquid with T to 300 K and $P \leq$ 500 bar
- Reaction Calorimetry with $T$ to 400 K and $P \leq$ 20 bar.
- Mechanistic validation of reversible pathways in $Mg(BH_4)_2$
- Validation of calculated enthalpy of hydrogenation of triazine.

BERKELEY LAB

ST133

- IR spectroscopy (DRIFTS) with precise $H_2$ dosing at $T$ = 10-300 K, $P \leq$ 100 bar
- Accurate modeling of $H_2$ adsorbed within porous materials
- Mechanistic validation:
  - can exposed cations in adsorbents reach target of $\Delta H = -15$ kJ/mol?
  - is it possible to adsorb two, three, or four $H_2$ per metal cation?

NIST

ST135

- Neutron diffraction with precise $D_2$ dosing at $T > 5$ K, $P \leq$ 100 bar
  - Determine crystal structures
- Inelastic neutron scattering at $T > 5$ K, $P \leq$ 100 bar
  - Understand the local environment for chemical-H and physisorbed-$H_2$
- Other neutron methods as applicable as applicable

# Approach: The Role of NREL

**Validation**

- $H_2$ storage materials performance metrics
- Computational methods for predicting hydrogen storage properties

**Characterization**

- the physiochemical properties of emerging hydrogen storage materials
- new concepts for hydrogen storage mechanisms

- **Validation and characterization of sorbent physiochemical properties**
  - PCT analysis with P≤ 200 bar $H_2$ and temperature control from 50 – 350K
  - Thermal Conductivity (TC) with $T$ = 77 - 400 K, $P \leq$ 100 bar $H_2$/He
- **Mechanistic validation:**
  - can exposed cations in carbon-based sorbents reach target of $\Delta H$ = –15 kJ/mol?
  - is it possible to control sorbent desorption temperature?
- **Validate computational predictions of $H_2$ binding energies and capacities.**

# Approach – characterization

## Thermal Conductivity (FY 16), Poster ST014

- **Design and construct a TC apparatus capable of measuring the thermal conductivity of hydrogen storage materials under expected operating conditions:**
  - Temperature range from 77 K to 400 K
  - Pressures up to 100 bar hydrogen
  - Capable of measuring pucks and powders and small-volume samples (down to ~ 0.5 $cm^3$)
  - Develop measurement hardware and "best practices" procedures (LANL)

## PCT Analysis (FY 16 - 17) Poster ST014

- **Develop recommended PCT measurement, analysis and reporting protocols**
  - Volumetric and Gravimetric capacities of hydrogen storage materials
- **Design and construct a modified variable-temperature PCT Apparatus**
  - Variable temperature range from 50 K to 350 K
  - Capable to achieve up to 200 bar hydrogen overpressure
  - Ability of measuring sample sizes from 200 mg to >1 gram.

# Approach - validation

- **Gravimetric and Volumetric capacities (Poster ST014)**
  - **Validation of storage capacities for external samples**
  - **Inter-laboratory Volumetric Adsorption Measurement Study**
    - **15 participants from Industry, Academia and National Laboratories in USA, Europe, Asia and Oceania. (Prelim results at poster session)**
  - **Consensus on reporting volumetric capacities**

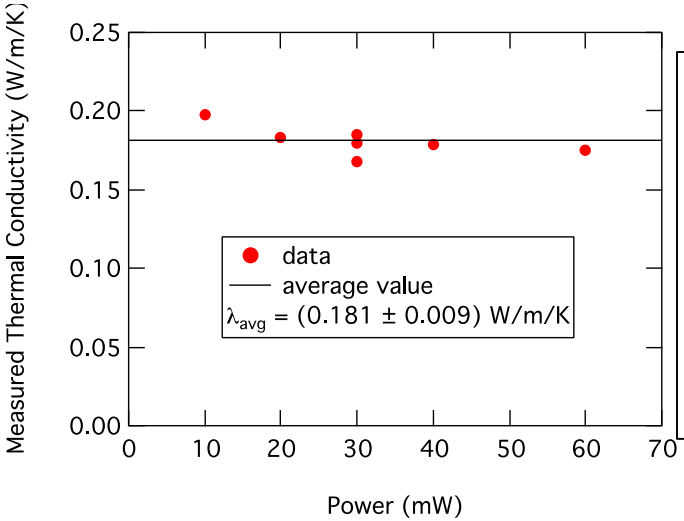
- **New approaches and materials that would enable $H_2$ uptake and release at ambient temperatures and moderate pressures, (i.e. validating theoretical models).**
  - **Control hydrogen desorption temperature with metal center**
    - **Multiple hydrogen molecules per metal center**
  - **Modified pore structure/chemistry to enable control of the hydrogen desorption temperature (thermodynamic and kinetic)**
    - **Control physisorption properties of high surface area sorbents**

# Accomplishments: Thermal Conductivity Apparatus Design and construction (Poster ST014)

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

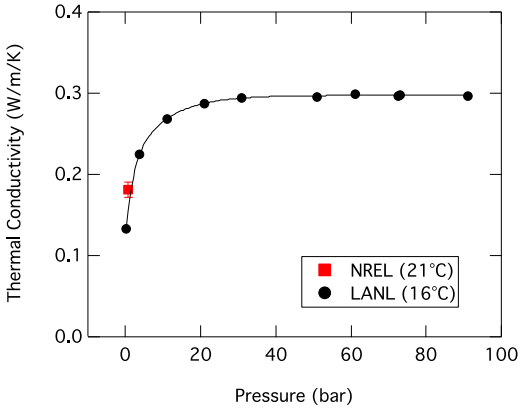
- ***Transient Plane Source Technique***
- 77 K to 400 K
- up to 100 bar
- capable of measuring pucks and powders (down to ~ 0.5 $cm^3$)

## MOF-5 Measurements




Mathematical model fit the data well.

Reproducibility with different applied power.




MOF-5 Room temperature
He at 1 bar
Isotropic measurement
Matched LANL results

# Accomplishments: Cryogenic Measurements (ST014)

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

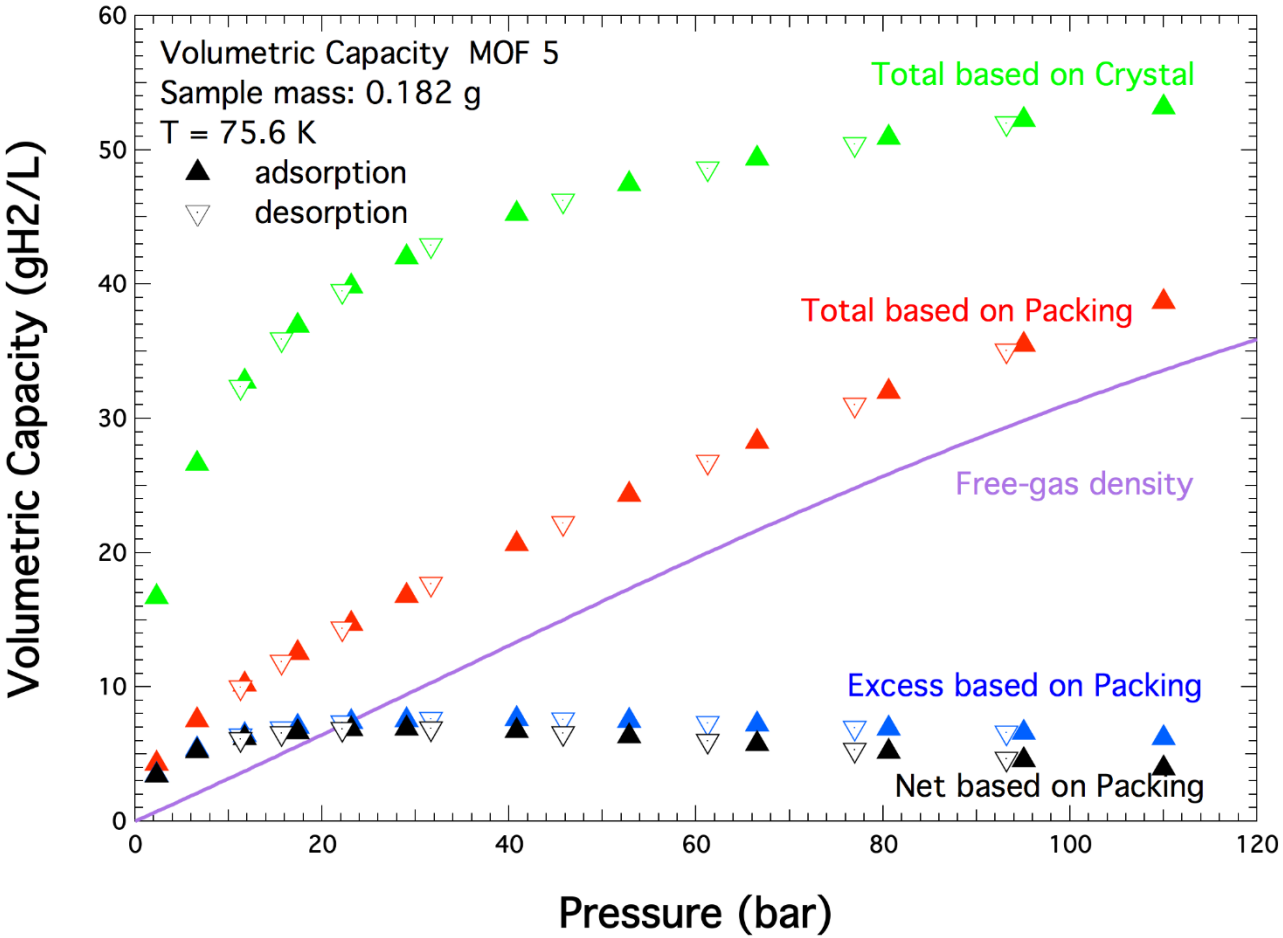
| T (K) | Gas | Pressure (Torr) | K Measured (W/m-K) | K Accepted (W/m-K)† | Percent Deviation |
|---|---|---|---|---|---|
| 75.6 | He | 615 | 0.47 | 0.45 | +4.4% |
| 75.6 | He | 210 | 0.46 | 0.45 | +2.2% |
| 295 | He | 615 | 1.15 | 1.1 | +4.6% |
| 295 | Air | 615 | 1.12 | 1.1 | +1.8% |

- 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)

# Volumetric Results Depends on Assumptions

## Normalization affects volumetric data




Graph shows the <u>same</u> raw data calculated with different $H_2$ capacity determinations.

**Note the difference between the Total capacities based on crystalline and packing densities.**

# Accomplishment: Inter-laboratory Volumetric Capacity Hydrogen Adsorption Measurement Study

$H_2$ sorption measurements on two distinct sorbent samples measured at 77K and ambient temperature.

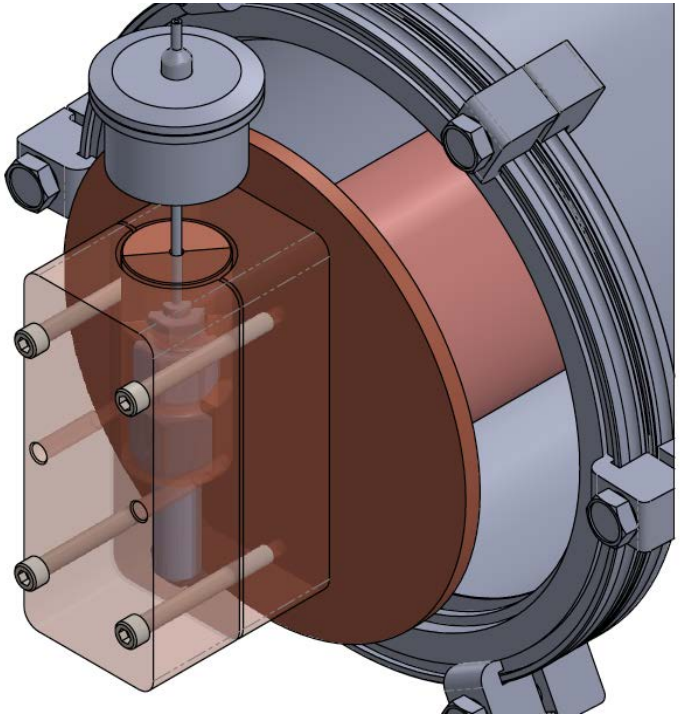
- Includes both excess and total volumetric capacities
- Builds on smaller previous study focused on excess gravimetric capacity

  (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
- 15 confirmed participants (including NREL) Includes Academia, Industry and National Laboratories from USA, Europe, Asia and Oceania.

(Poster ST014) for preliminary results

# Accomplishment: Variable Temperature PCT Cryostat Design

**Progress toward FY 17 Milestone**



Modification of one of our current PCT instruments includes a cryo-cooler for controlling the sample temperature from 50K to 350K with $H_2$ pressures ≤ 200 bar .

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

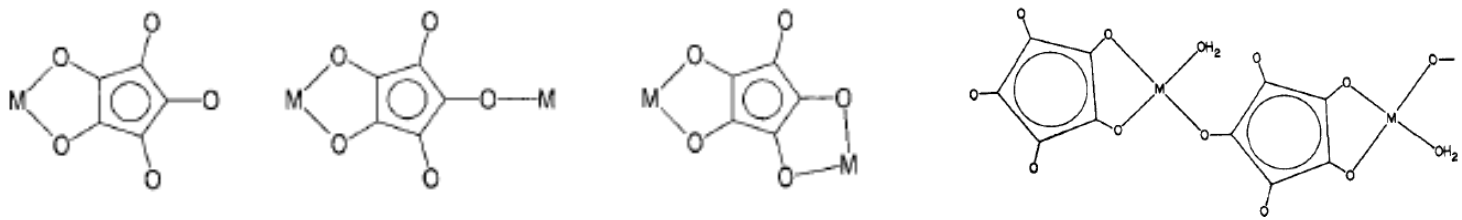
**This design expands NREL's core characterization capabilities to include PCT measurements from 50 to 350K and enable the determination of the heats of adsorption.**

# Accomplishment: Effect of metal cation on hydrogen desorption temperature

**Oxocarbon ions are cyclic compounds of the general formula $(C_nO_n)^{2-}$**

**2 – oxalate 3 – deltate 4 – squarate 5 – croconate 6 – rhodizonate**

**The electronic delocalization provides the possibility of pi-stacking interactions between the oxocarbon rings and unusual electronic and vibrational properties.**

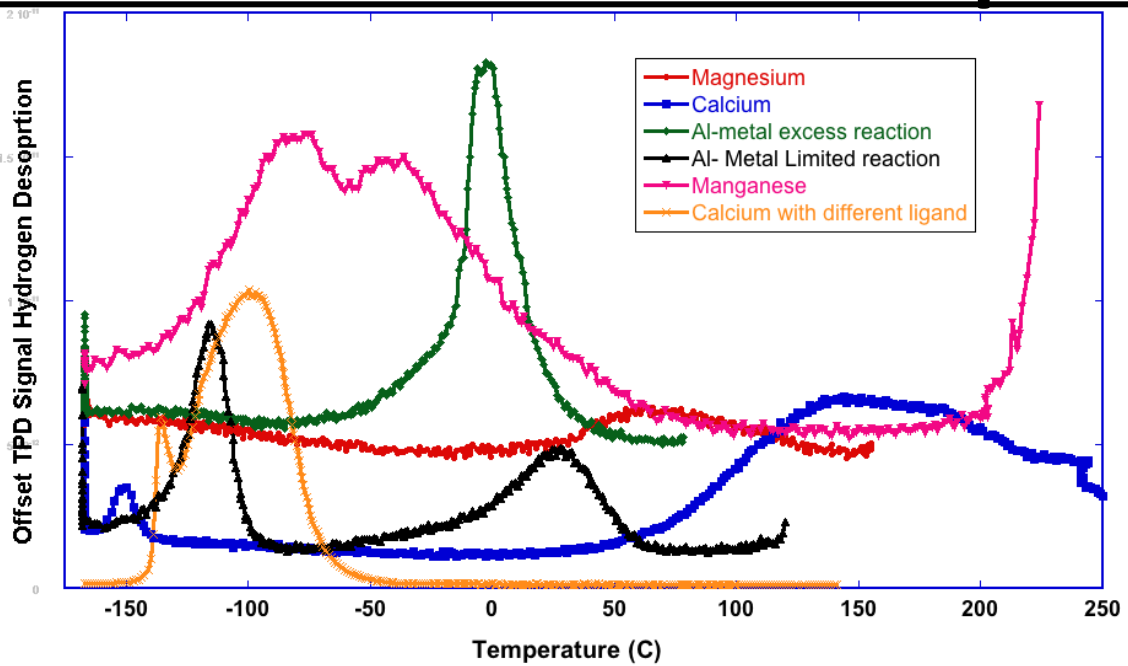


**Synthesis:**

- **Reaction of the respective metal nitrate or chloride with the sodium oxocarbon salt in water, methanol and/or anhydrous methanol.**
- **Various ratios and concentrations of reagents were used in attempts to alter the binding interaction and chain lengths.**
- **Transition metal complexes are predicted to be high-spin.**

**Metals investigated to date include: Manganese, Magnesium, Beryllium, Calcium, Nickel and Aluminum.**

# Effect of Metal on Desorption Temperature




| Metal/Ligand | Desorption Temperature (K) | Gravimetric capacity (1 bar) %w/w approximate |
|---|---|---|
| Be/mixed oxalate | 150 K | <0.2% |
| Al/mixed oxalate | 125 - 175 K (small pk 273K) | 0.1 – 0.3% |
| Ca/mixed oxalate | 150 – 225K | 0.4 – 0.8% |
| Mg/croconate | 340K | < 0.1% |
| Ca/Croconate | 350 – 473 K | < 0.1% |
| Al/Croconate (a) | 265 – 290 K | 0.5 – 0.8% |
| Al/croconate (b) | 140 – 170 K, 273 – 320K | 0.1 – 0.3% |
| Mn/Croconate | 200 K and 225 K (2 peaks) | 0.2 – 0.4% |

**Demonstrated the ability to alter the hydrogen desorption temperature**

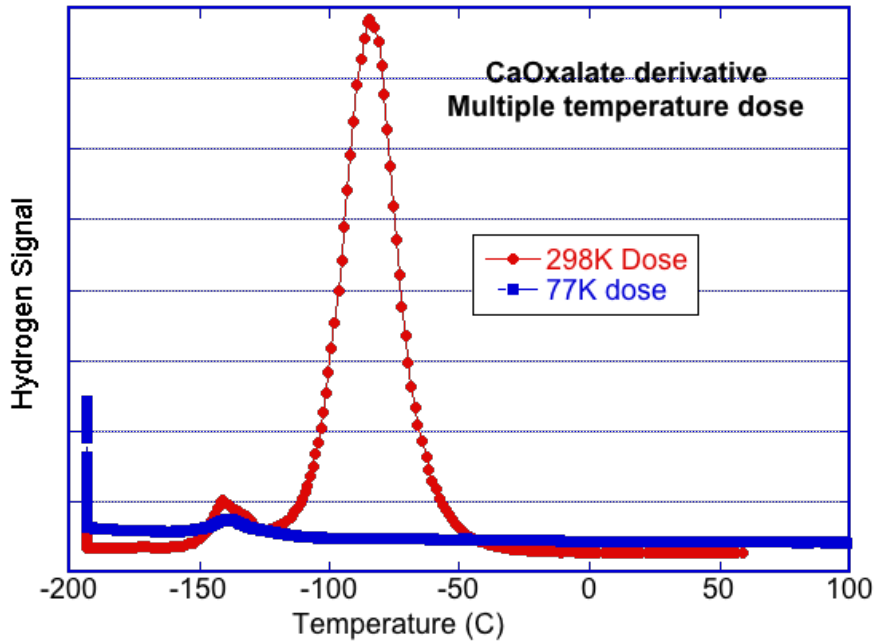
**Will now determine extent of kinetic and thermodynamic contributions**

**Will now work to improve capacity.**

# Accomplishment: Ultramicroporous materials

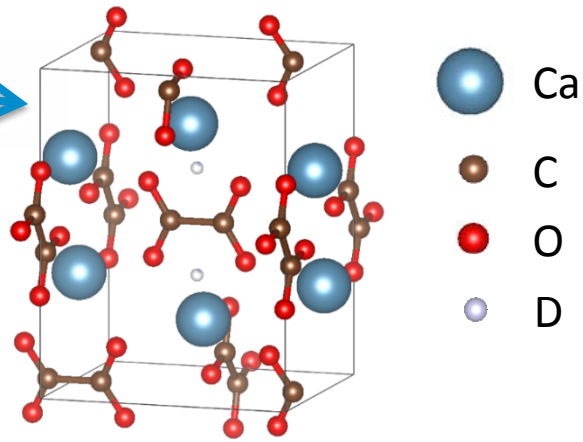
**CaOxalate Derivative**.

- Must dose at temps above 175K and pressures >250 torr
  - Established in joint PNNL/NIST/NREL efforts
- BET surface area 4 $m^2/g$, yet capacity approaches 1% w/w (≈1.5% theoretical for 1 $H_2$/Ca)
- Collaborative effort with NIST established no structural changes with temperature
- Appears is first ultramicroporous material with high (150K) desorption temperature (past materials were at 50 K, Hirscher, 2009 MgFormate)
- Kinetic versus thermodynamic effect
  - Binding energy vs. "diffusion" limits
- Need to establish pore sizes
  - Is their a structure change with temp
  - Metal or ligand "trapped" hydrogen
- Modeling (working with LBNL)

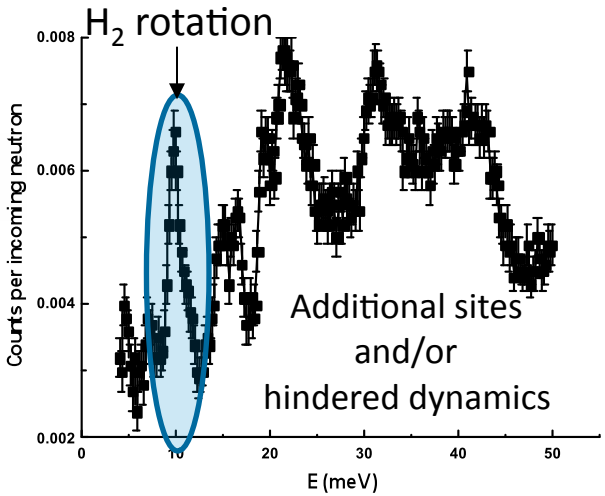


# Accomplishment: Neutron characterization of calcium oxalate derivative (ST135)

- **Neutron Powder Diffraction**
  - Anhydrous calcium oxalate derivative confirmed as dominant phase
  - Changes in relative intensity of reflections upon dosing with $D_2$ reveal crystallographic planes in which hydrogen resides
  - Accurate refinement and precise determination of hydrogen adsorption sites complicated by additional crystal phases

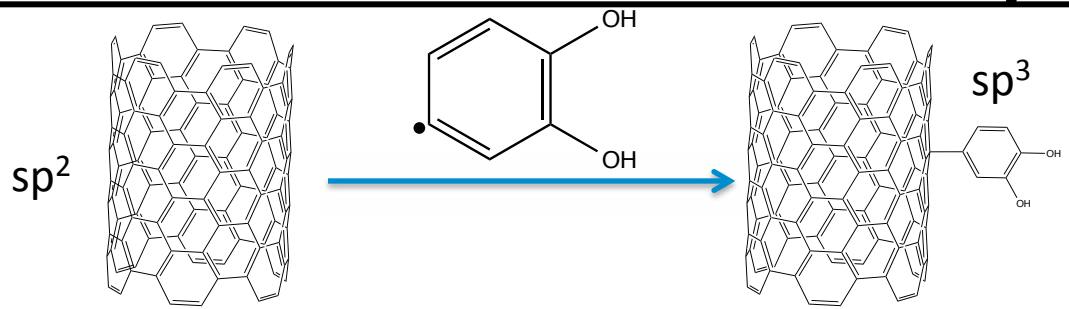


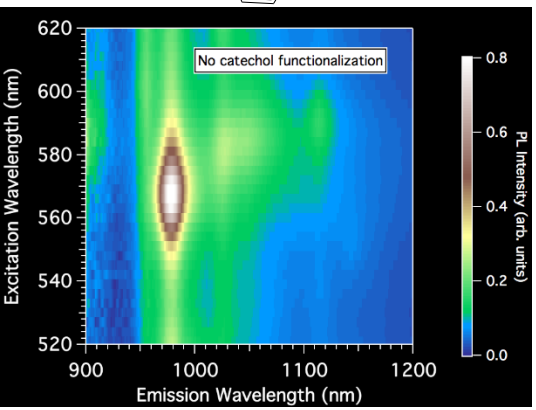

- **Inelastic neutron spectroscopy**
  - Sensitive almost exclusively to hydrogen
  - Loading pressure has a strong influence on adsorption properties
  - Adsorption of $H_2$ at atmospheric pressure suggests multiple binding sites and/or hindered dynamics

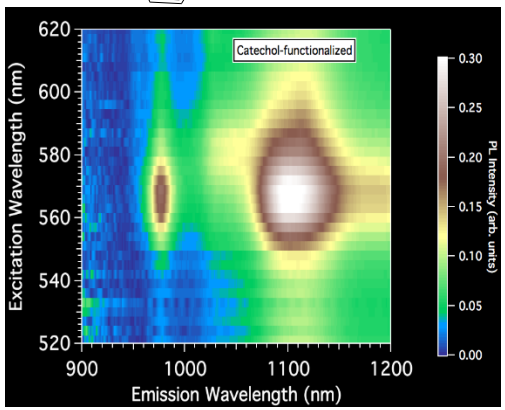


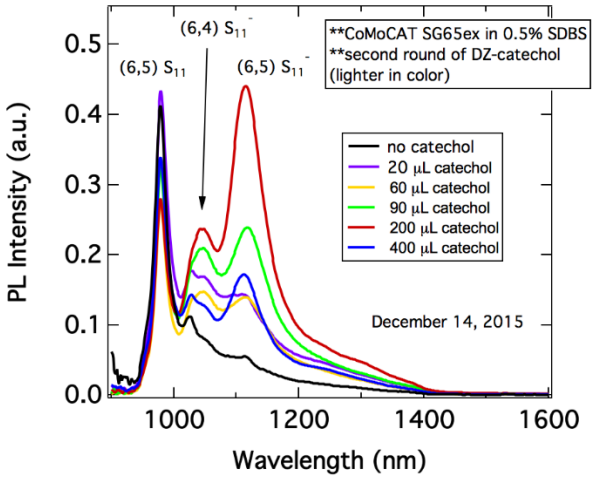

Neutrons locate adsorbed $D_2$ possibly in micropores

# Accomplishment: Modified sorbent pore structure/chemistry



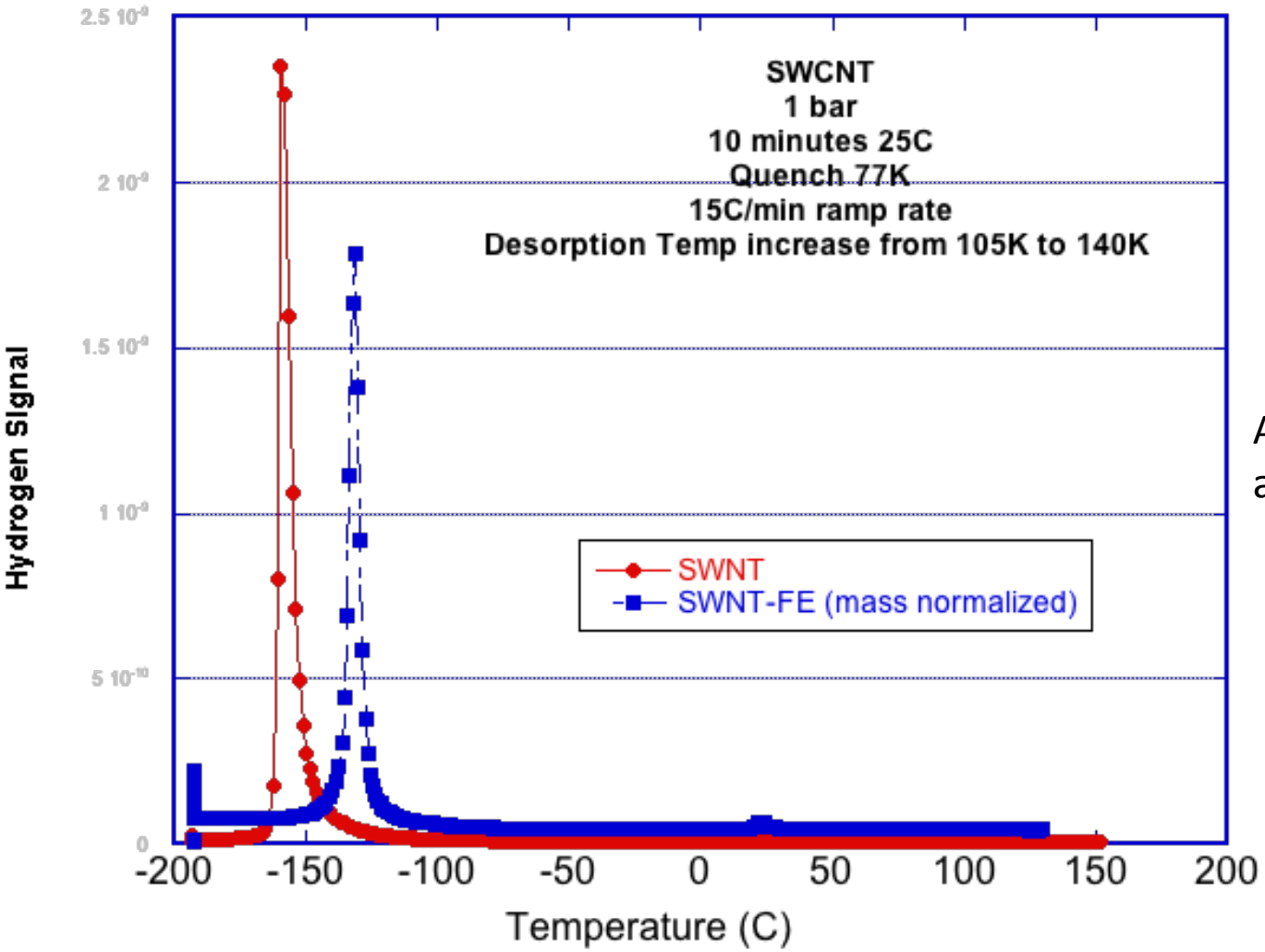




PL dominated by emission at 990nm from $sp^2$ for pristine SWCNTs

PL intensity by emission at 1100nm from $sp^3$ SWCNTs after modification allows for determination of extent of catechol incorporated

PL intensity plots allow for determination of catechol substitution levels.

# Accomplishment: Increase Desorption Temperature of SWCNT sorbent




Approx. 1%w/w capacity at 1 bar)

# Internal Collaboration Efforts

- **Collaboration of LBNL and NREL on verifying hydrogen adsorption isotherms, measuring thermal conductivities, measuring temperature programmed desorption data. (joint paper planned)**
- **Collaboration of LBNL, NREL and PNNL on measuring hydrogen adsorption in multiple materials using solid state NMR spectroscopy. (several papers planned in near future)**
- **Collaboration of LBNL and NIST on characterizing hydrogen adsorption in framework (MOFs) materials using neutron diffraction and neutron scattering spectroscopy. (joint paper submitted)**
- **Collaboration of NREL and NIST on characterizing ultramicroporous materials using neutron diffraction and neutron scattering spectroscopy. (joint paper planned)**
- **Collaboration of NREL and LBNL on the modeling of hydrogen sorption in hybrid ultramicroporous materials**
- **Collaboration of NREL with NIST and LBNL to characterize various materials at the APS facility. (joint papers planned)**
- **Collaboration of PNNL and NIST: dynamics models to fit experimental NMR data using insight from QENS and INS, (planned)**

# Collaborations with HyMARC

- NIST Collaborations with SNL: Developing Spectroscopic Signatures for $Mg(BH_4)_2$
- NIST Collaborations with SNL: Determining products of hydrogenated $Li_3N$ in nanoporous carbon
- Collaboration of PNNL and Sandia: sample exchange: standards for x-ray: $B_3H_8$, $B_3H_8$, $B1_0H_{10}$, $B_{11}H_{14}$, a mix of $B_{11}H_{14}$ + $B_9H_{14}$ + $B_3H_8$, dehydrogenated $Mg(BH_4)_2$ and $B_{12}H_{12}$
- Collaboration of PNNL and LLNL: Comparison of $^{11}B$ NMR for release of $H_2$ from $Mg(BH_4)_2$ with $H_2$ uptake by $MgB_2$
- Collaboration of NREL and HyMARC (LLNL) for the modification of advanced carbon based sorbents by solution and PVD techniques. (exchange of materials and techniques to verify applicability)

# Remaining Challenges and Barriers

- **Achieving more direct collaborations with HyMARC Team**
- **Achieving a collaborative balance with the new FOA initiated projects**
- **Designing autonomous software for both the advanced TC and PCT systems**
- **Achieving an International consensus on reporting volumetric and gravimetric capacities**
- **More interaction of theorists and experimentalists.**
- **Application of the advanced NMR, DRIFTS and Neutron capabilities to a broad base of sorbent materials**
- **Exhibiting control over kinetics in sorbent systems**
- **Exhibiting control over thermodynamics in sorbent systems**
  - Binding energies
- **Improved capacities of multi-hydrogen systems**
  - Increase to beyond two hydrogen molecules per metal center
- **Control over "useable" hydrogen stored in sorbent materials**
- **Improved cost considerations**

# Proposed Future Work

**TC Next steps:**

- **Measurements at controlled temperatures down to 77 K**
  - Isotropic versus anisotropic
- **Measurements with pressurized $H_2$ up to 100 bar**
- **Autonomous software completion**

**PCT Next Steps**

- **Analyze data and publish results from the inter-laboratory volumetric hydrogen measurement study**
- **Validate measurements for hydrogen sorption.**
- **Develop new capabilities for measuring the hydrogen sorption with increased temperature range (50K – 350K).**
  - Need to finalize system design of cryostat and sample holder for VT- PCT system
  - Develop new Lab-view instrument software
  - Validate isosteric heat of adsorption measurement

# Proposed Future Work

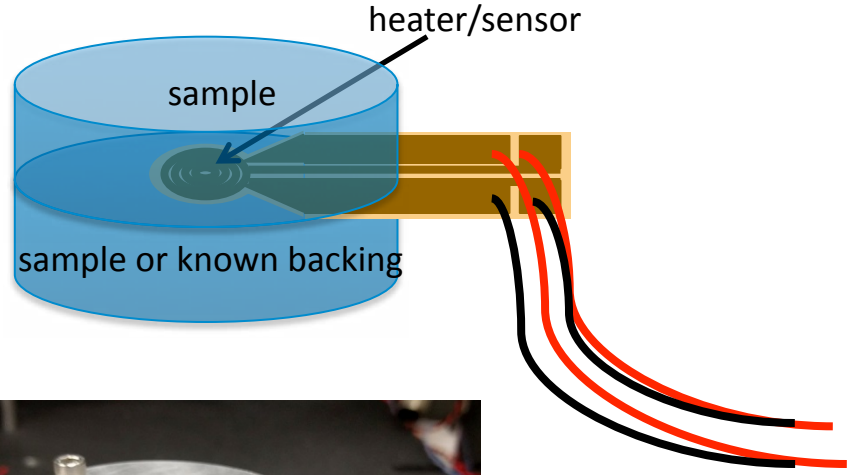
- **Modeling of various oxo-carbon materials (with LBNL)**
  - Validate models
- **Establish position of metal site within SWCNT-catechol materials (with NIST)**
- **Modify high surface area carbon materials with catechol (Materials from NREL and HyMARC (Ted Baumann))**
- **Identify position of hydrogen within oxo-carbon materials (NIST, PNNL, LBNL)**
- **Establish further control over metal-sorbent synthesis materials for enhanced capacity.**
  - Currently at approximately 1% w/w for model materials

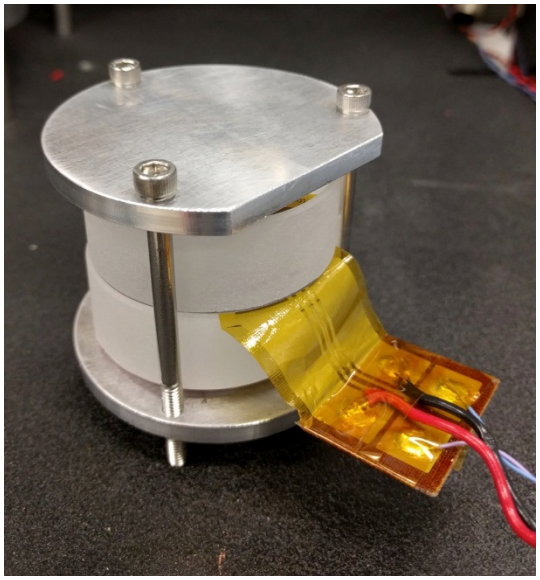
# Mandatory Summary Slide: Highlights

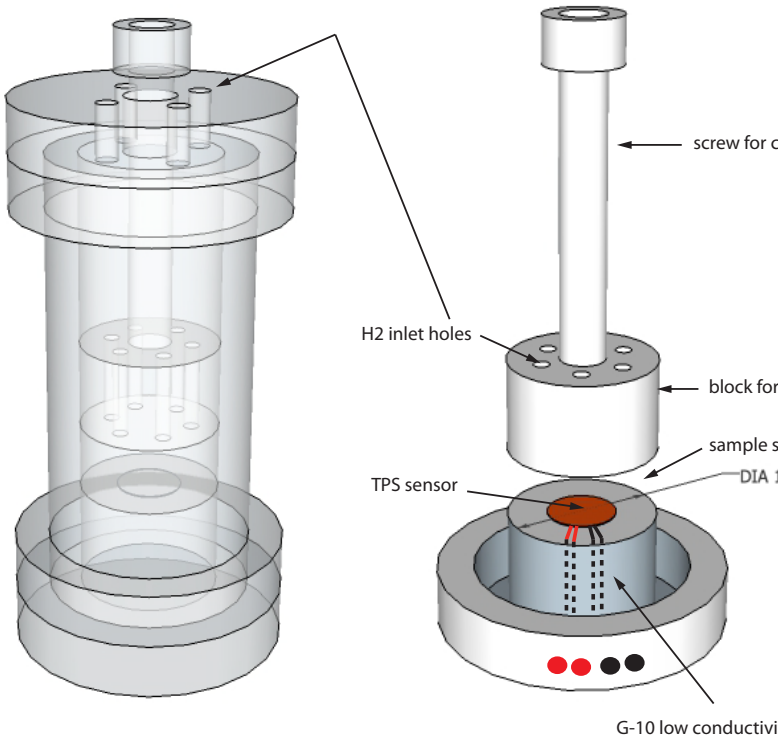
- **Kick-off meeting October 10, 2015 at LBNL, All participants present**
- **Joint NDA with HyMARC completed October 2066.**
- **Joint meeting with HyMARC at NREL November 3-5, 2015**
- **Joint Tech Team meeting with HyMARC, April 20-21, 2016**
- **Monthly conference calls (more often individual interactions)**
- **New Hires**
  - NREL, 2 postdocs, 0.5FTE
  - PNNL, 1.5 postdoc
  - LBNL, 3 postdoc, 3 graduate students
- **New advanced characterization and materials performances were observed at LBNL, PNNL, NIST and NREL. Several of the most important results are summarized herein.**
  - **NREL**
    - built and written software for an advance TC instrument for measuring the thermal conductivity of $H_2$ storage materials under operating conditions.
    - initiated a very important round robin volumetric study
    - completed designs for a new advanced variable temperature PCT system
    - synthesized novel catechol derivatized nanostructured carbon materials
    - exhibited control of desorption temperatures in metal-oxocarbon systems. (Collaboration with NIST, LBNL and PNNL)
  - **LBNL**: observed 2 hydrogen molecules on a metal center as characterized by NIST within framework material (paper submitted) (ST133)
  - **PNNL:** enhanced kinetics of the hydrogen interaction with borohydride materials (collaboration with HyMARC and Univ of Hawaii)(ST132)
- **All milestones on track and/or completed.**
- **11 publications (published, in-press or submitted)**
- **3 Records of Inventions submitted to protect IP.**

# Technical Back-up slides

# Approach: TPS Sample Holders



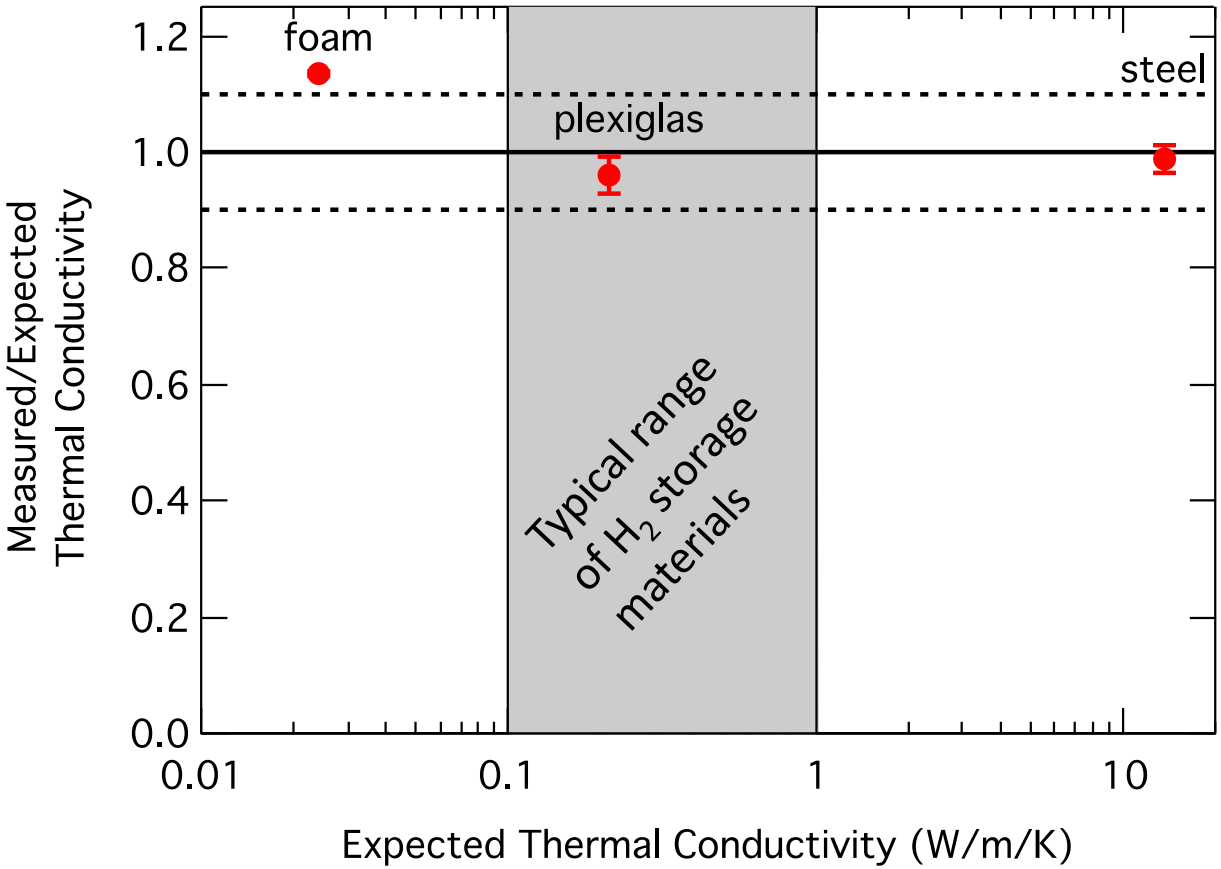






Possible design for powder samples.

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

# Accomplishments: Measurement Validation



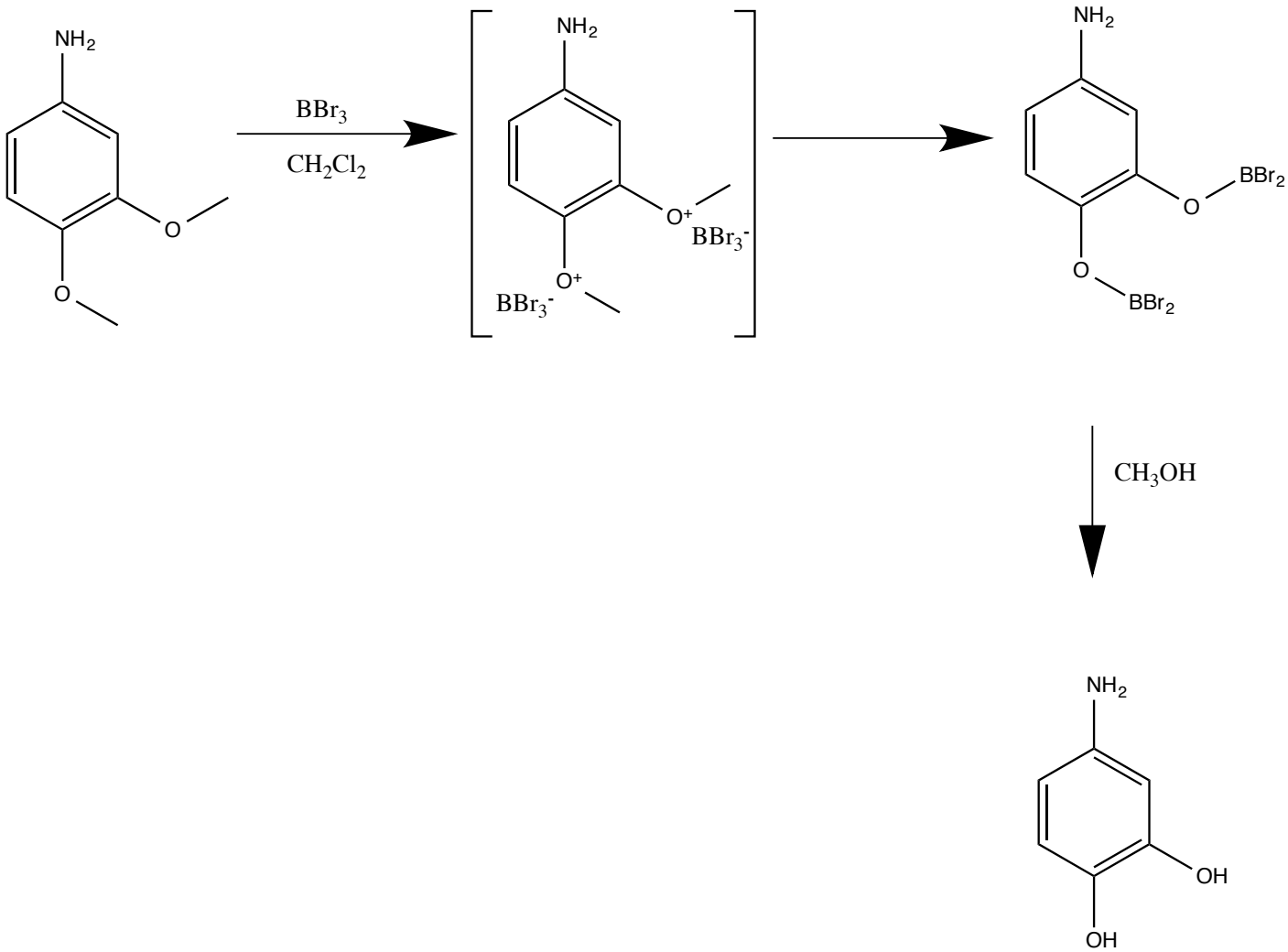

Reference materials:

- Stainless Steel
- Plexiglas
- Foam Insulation

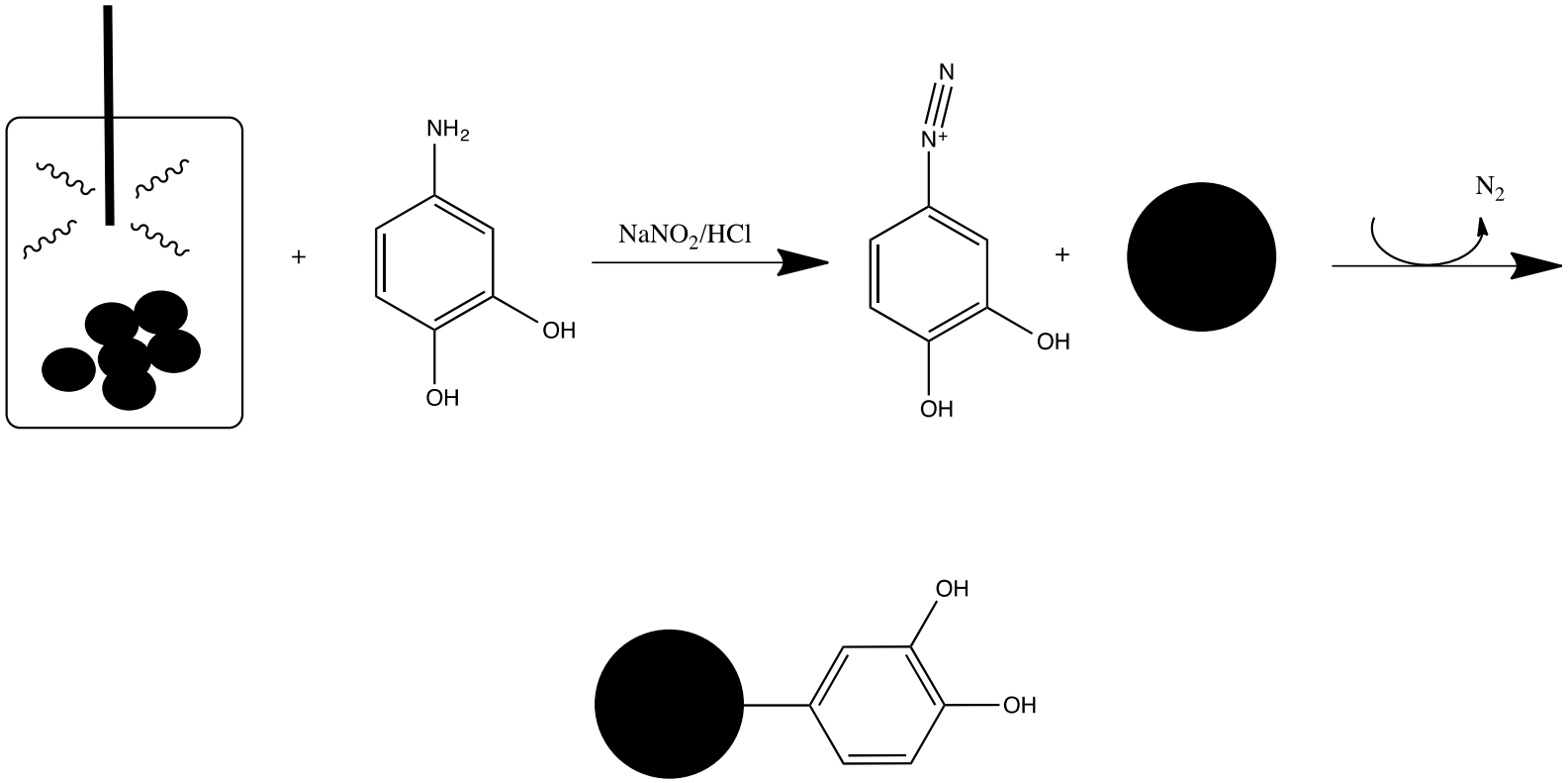
(room temperature, atmospheric pressure)

**Good agreement over 3 orders of magnitude**

# Accomplishment: Preparation of 4-aminocatechol



# Accomplishment: Functionalization of carbon with catechol




= CNT, Black Pearls, "PEEK", etc.