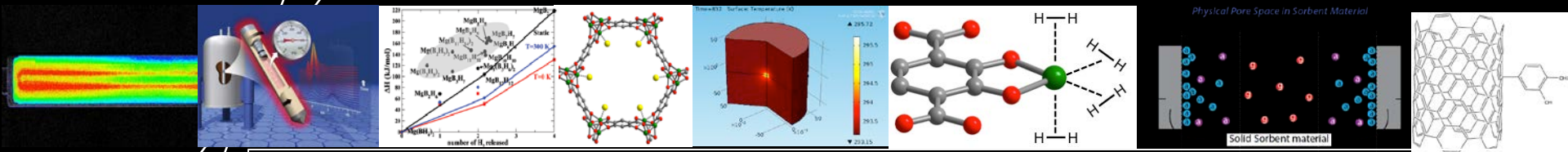
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

HySCORE

Project ID ST131

H_2 Storage Characterization and Optimization Research Efforts (HySCORE)

NREL's Technical Efforts



DOE-FCTO AMR Presentation

June 7, 2017

NREL Team: Rory Andrykowski, Jeff Blackburn, Wade Braunecker, Steve Christensen, Arrelaine Dameron, Mira Dimitrievska (NIST), Katie Hurst, Ellis Klein, Noemi Leick, Michele Olsen, Phil Parilla, Steve Robbins, Jacob Tarver (NIST), Jerry Tynan, Tom Gennett (PI)

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

Pacific Northwest NATIONAL LABORATORY

NIST Center for Neutron Research

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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

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

Total Team Budget: (HySCORE): $8.2M

Federal Share:

NREL: $2.6M

LBNL: $2.4M

PNNL: $2.4M

NIST: $0.8M

NREL Funds Spent: ~$1.2M

(Estimated as of 3/31/17)

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

IEA-HIA Task 32 Participants

Thesis Corporation, Justin Lee

Univ. Wyoming, Bruce Parkinson

Energy Materials Network:

Hydrogen Materials – Advanced Research – HyMARC and HySCORE

Individual projects via FOA

- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**

Core National EMN Team

Characterization and Validation Team

- **Characterization Resources**
  - Validation of Performance
  - Validation of "Theories"
- **"User-facility" for FOA projects/HyMARC**
- **Characterization Method Development**

Relevance: HySCORE Initiative

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)**

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

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Relevance: HySCORE Materials Goals

HySCORE

- **New concepts for H_2 storage mechanisms**
  - ***Provide accurate computational modeling for H_2 adsorbed in porous materials***
  - ***Develop and characterize materials with validated coordinately-unsaturated metal centers, and/or advanced hydrides and/or framework and/or templated materials and/or carbon-sorbents within the hydrogen storage matrix that result in experimental control of:***
    - ***Desorption temperatures***
    - ***Volumetric and gravimetric capacities***
    - ***Kinetic and thermodynamic contributions***
    - ***Materials intrinsic properties***
    - ***Sorption and delivery pressures***
- **Demonstrate by end of FY 18**
  - ***Volumetric capacities in excess of 40 g/L, to approach the doubling of energy density***
  - ***Targeted enthalpies in the ideal range of 12-20 kJ/mol***
  - ***Acceptable gravimetric capacities and the ability to deliver on-demand H_2 at an appropriate rate and pressure for hydrogen fuel cell vehicles at temperatures from 150-225K and initial overpressure <100bar.***
- **Ultimate Goal**
  - ***5.5 wt. % H_2 total Gravimetric capacity***
  - ***50 g H_2/L total Volumetric capacity***
  - ***Operating temperature from –40 to 60 °C***
  - ***Maximum overpressure 100 bar***

Approach: All Partners

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ST131, ST014

- Validation and characterization of sorbent physiochemical properties
  - **Advanced PCT analysis**
  - **Thermal Conductivity (TC)**
- Mechanistic validation:
  - **Carbon-based sorbents with $\Delta H \approx$ -15 kJ/mol.**
  - **Control sorbent desorption temperature via thermodynamics and/or kinetics**.
    - Via materials development/modification
- Validate computational predictions of H_2 binding energies and capacities

BERKELEY LAB

ST132

- IR spectroscopy **(DRIFTS)** with precise H_2 dosing
- Accurate **modeling** of H_2 adsorbed within porous materials
- **Advanced framework materials**
- Mechanistic validation:
  - $\Delta H = -15$ kJ/mol?
  - **is it possible to adsorb two, three, or four H_2 per metal cation?**
- Validate computational predictions of H_2 binding energies and capacities

Pacific Northwest NATIONAL LABORATORY

ST133

- **NMR (i) solid state with precise H_2 dosing; (ii) in-situ MAS (iii) variable pressure liquid**
- Reaction Calorimetry
- **Mechanistic validation of reversible pathways in $Mg(BH_4)_2$**
- Validation of calculated enthalpy of hydrogenation of liquid carriers.

NIST Center for Neutron Research

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 chemisorbed - H and physisorbed - H_2
  - Other neutron methods as applicable

Approach: Characterization at NREL

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Thermal Conductivity (ST014)

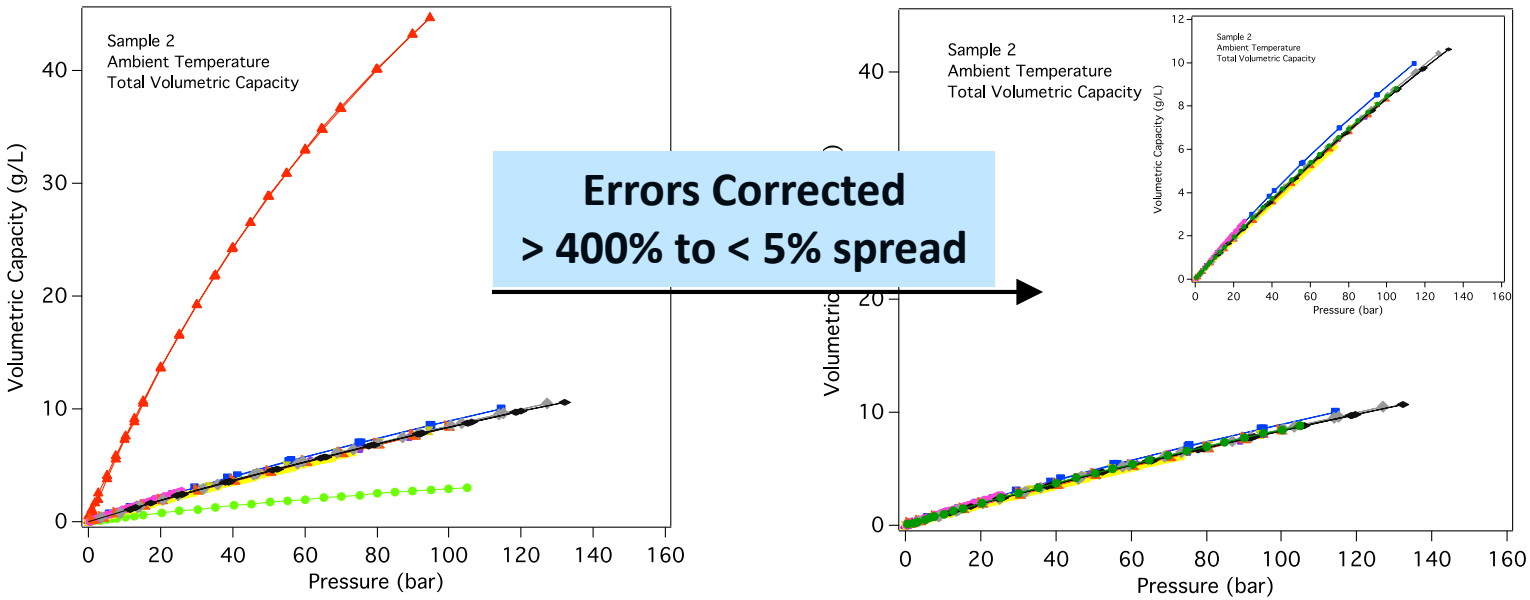
- **Developed a TC apparatus capable of measuring the thermal conductivity of hydrogen storage materials under expected operating conditions:**
  - Temperature range from 40 K to 400 K
  - Pressures up to 100 bar hydrogen
  - Multiple gas options
  - Capable of measuring pucks and powders and small-volume samples (down to ~ 0.5cm^3)
  - Develop measurement hardware and “best practices” procedures (LANL)

PCT Analysis (ST014)

- **Develop recommended PCT measurement, analysis and reporting protocols**
  - Volumetric and Gravimetric capacities of hydrogen storage materials
- **Developing 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.

Accomplishments: Inter-laboratory Volumetric Capacity Hydrogen Adsorption Measurement Study

- Promoted valid comparisons of hydrogen-storage materials
  - ILS necessary to evaluate implementations of protocols
- Decreased irreproducibility due to systematic and "black box" errors
  - NREL gives direct feedback on data
- Determining a "natural" spread of data from instrument and operator variables



Phil Parilla presentation (ST014)

Approach: Materials at NREL

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- 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
  - Modify pore structure/chemistry to enable control of the hydrogen desorption temperature (thermodynamic and kinetic)
    - Control physisorption properties of high surface area sorbents

Approach: Modeling – Experiment synergistic activities (ST133)

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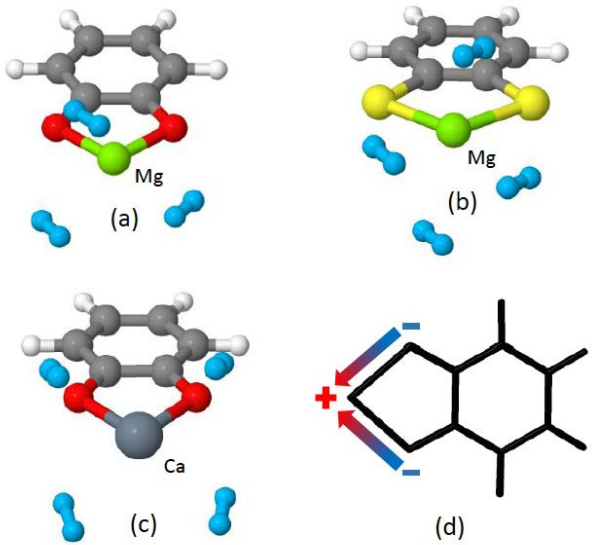
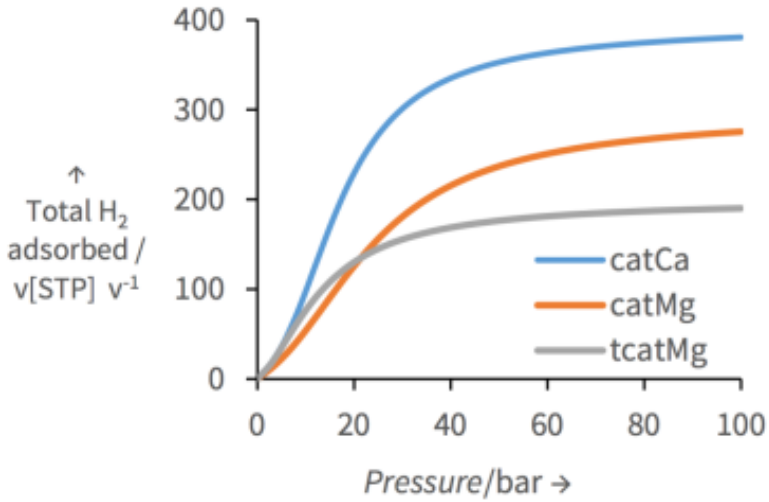
High-Temperature Hydrogen Storage of Multiple Molecules in Metalated Catechols (Cat-M)
[Tsivion, Ehud; Veccham, Srimukh Prasad; Head-Gordon, Martin ChemPhysChem (2017), 18(2), 184-188]



(a) Mg-catecholate (cat-Mg) (b) Mg thiocatecholate (tcat-Mg) (c) cat-Ca. The electrostatic field of the cat-M compounds is shown in (d).



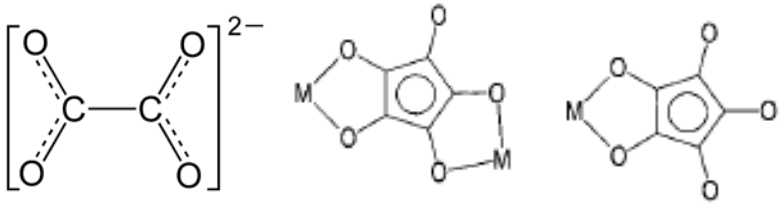
Predicted adsorption isotherms for the ***model*** complexes at 298K. The number of H_2 molecules adsorbed on a single metal site can be inferred by dividing the value of total H_2 adsorbed by 100.

- Initial Prediction: Cat-Ca can bind 4 H_2 with ΔE_{ads} between -14.7 and -15.9 kJ/mol
- NREL and LBNL are currently synthesizing target materials

Approach: Model materials (FY 16)

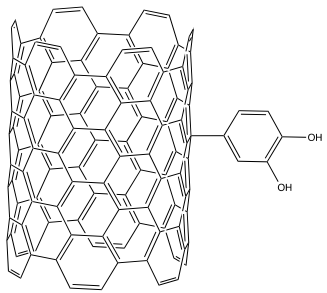
Oxocarbon ions general formula $(C_nO_n)^{2-}$

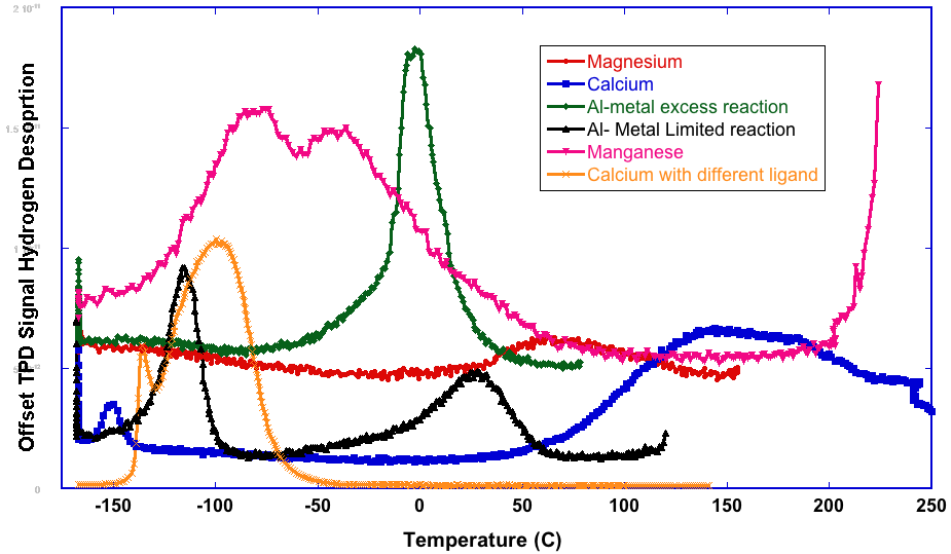
2 – oxalate 5 – croconate

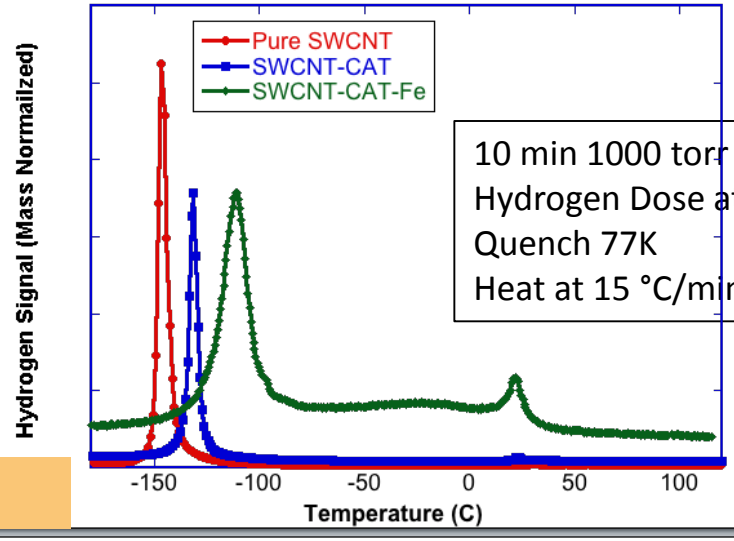


SWCNT – CAT - M

Dervatized SWCNT



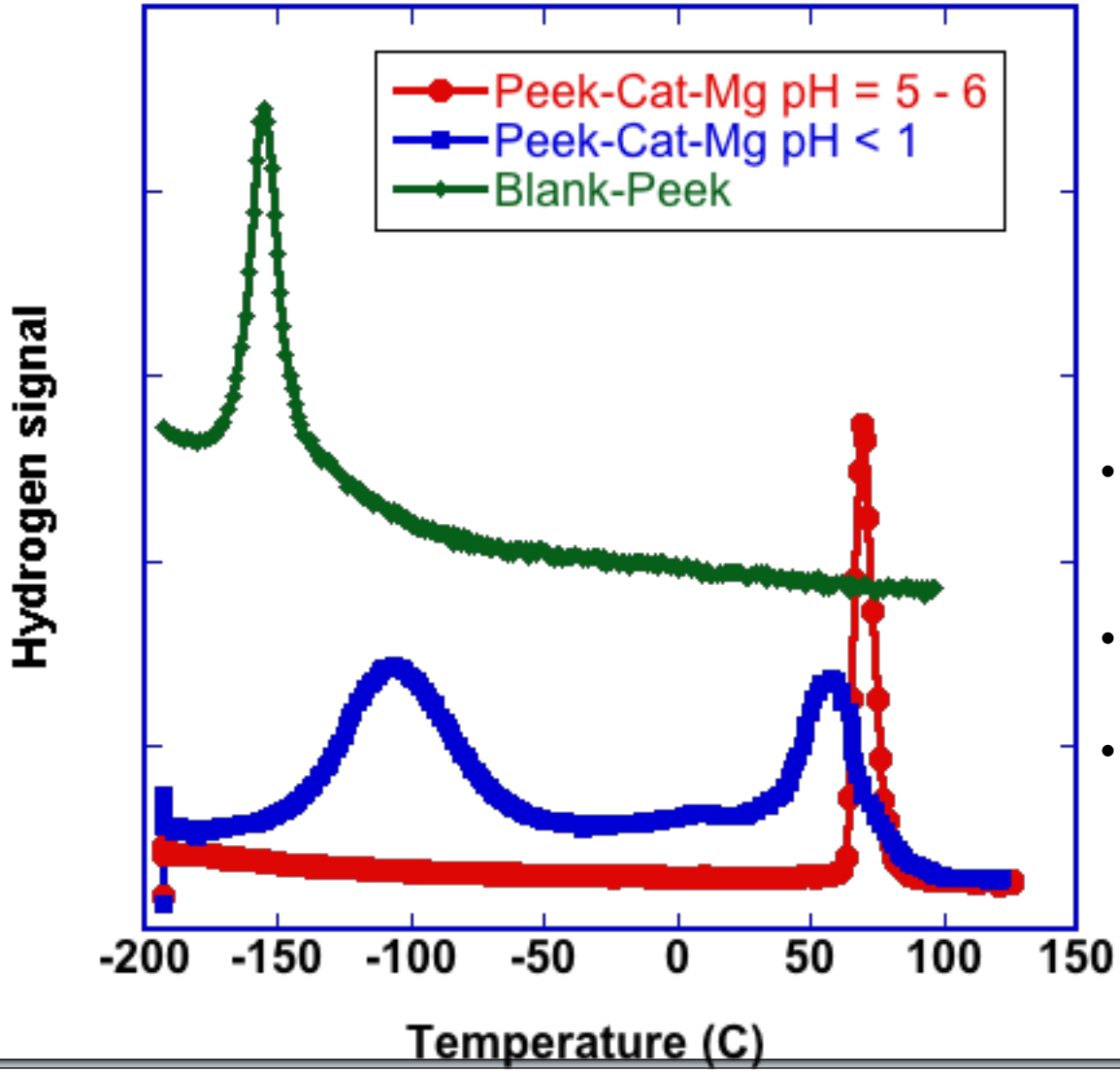




10 min 1000 torr
Hydrogen Dose at 298K
Quench 77K
Heat at 15 °C/min

Demonstrated ability to control H_2 desorption temperature

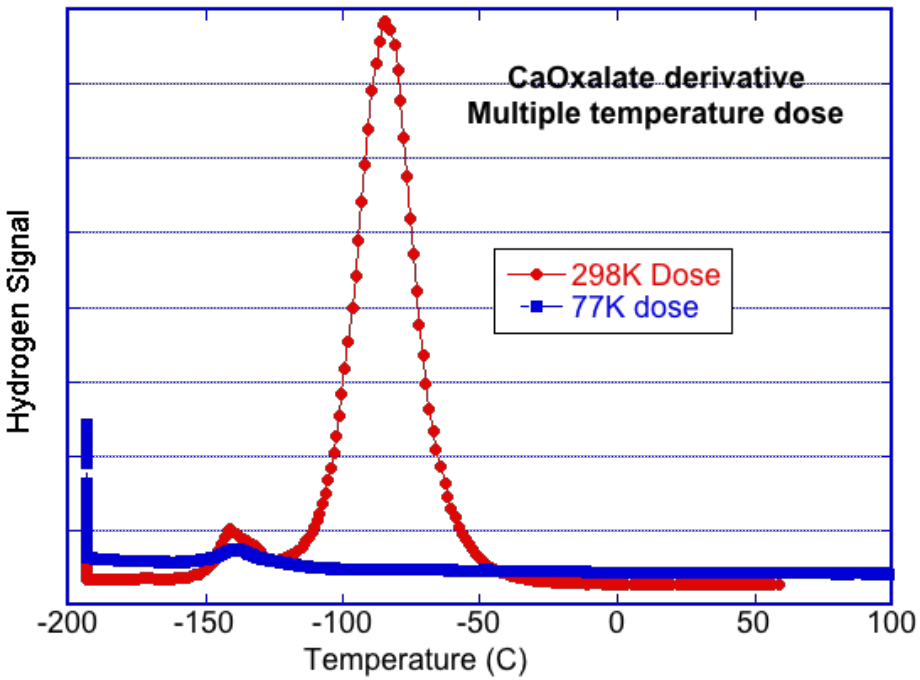
Accomplishment: Increase Desorption Temperature of nanocarbon–catechol-metal sorbent

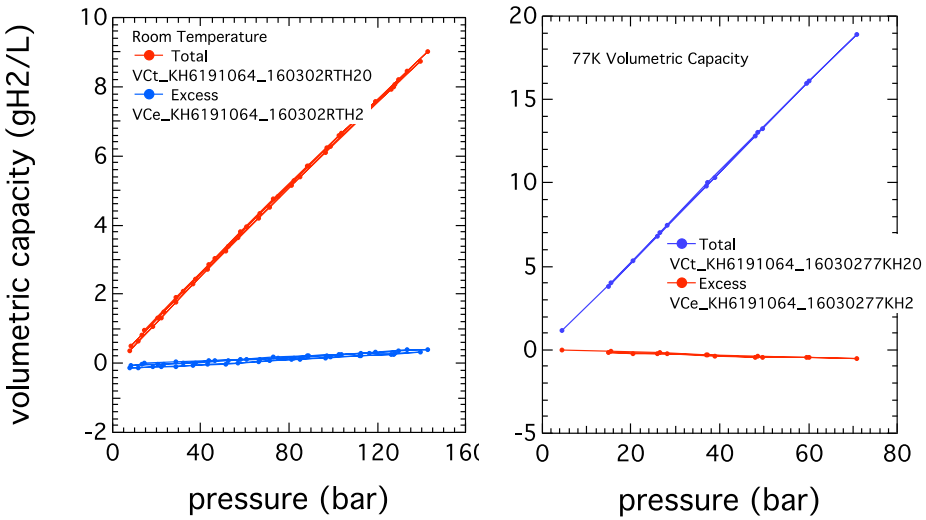


Pyrolyzed PEEK

- Can move H_2 desorption peak
  - Similar to model compounds
- Dependent on pH for metal incorporation?
- Need to improve control/level of catechol functionalization.

Accomplishment: Hydrogen Sorption, Calcium Oxalate





- 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 *for a 4 m^2/g* material**
  - **Mole counting experiment**
- At 77K there is zero adsorption after 6 hrs.

Accomplishment: Joint PNNL/NIST/NREL/LBNL efforts

Unexpected "*Ultramicroporous*" CaC_2O_4

- Must dose at temps above 175K and pressures >250 torr
  - BET surface area 4 m^2/g, yet capacity approaches 1.2% w/w
  - pores are smaller than the kinetic diameter of nitrogen not hydrogen
  - no structural changes with temperature
  - Alpha phase necessary?

- Appears as "*ultramicroporous*" material with high (150K) desorption temperature
  - Kinetic versus thermodynamic versus "disorder" effect
    - Binding energy vs. "diffusion" limits
    - Size exclusion
    - Surface phonon effect?

- Need to establish pore sizes (theoretical 4 - 6 angstroms)
  - No structure change with temp
  - No Isotope effect observed

- Theoretical predictions matched experiment (ST-133)

Approach: Effect of B or N incorporation on binding energy of H_2 on carbon (New Task)

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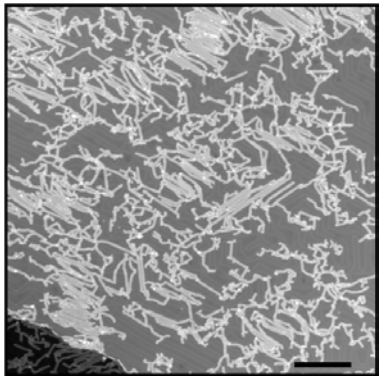
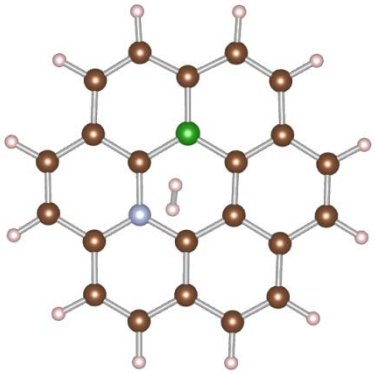
MILESTONE: Determine the viability of Boron and nitrogen doped materials for increased binding energy and capacities that could approach 2020 goal

a. Demonstrate reversible hydrogen uptake within a molecular solid-FLPs, sorption <30 minutes at 25 °C and desorption <60 minutes at 120 °C.

b. Synthesize a boron or nitrogen or co-doped sorbent with >8 atomic percent dopant incorporated into the backbone, with 2000 m^2/gram surface area and a hydrogen binding energy >12 kj/mole.





- **Can promising structures predicted by theory be synthesized?**
  - New theoretical evaluation (PNNL)
- **How does controlling the local structure of heteroatom impact binding energy?**
- **Can incorporation of 8% heteroatom be achieved on high surface carbon without agglomeration, BN or BC formation?**
- **Can we use ^{11}B NMR to look at the B/N doped carbon to better understand the B environment? BC and BN are well separated**
- **How do solution phase materials (PNNL) compare to solid state or physical deposition (NREL) material?**

Approach" Synthesis strategies for BC_x

HySCORE

[1]Yeom, D.-Y.; *et al.*, "High-Concentration Boron Doping of Graphene Nanoplatelets by Simple Thermal Annealing and Their Supercapacitive Properties". *Scientific Reports* **2015,** *5*, 9817.
[2] Shcherban, N.; *et al.*, Boron-doped nanoporous carbons as promising materials for supercapacitors and hydrogen storage. *J. Materials Science* **2017**, 52, 1523.

Selective incorporation of *sp*^{2}-like B for $BC_{x=0.87}$ by seeded B-doped-graphene CVD growth.

Step 1. *B-graphene* seeds [Ref. 1]:

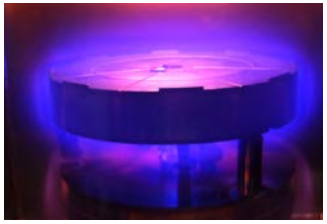
- B_2O_3 + Graphene Oxide
- Annealed at 1000°C / inert gas
- Yields 6 mol% B [Ref. 1]

Step 2. Plasma BC_x CVD [Ref. 2]:

- 400 W µ-wave plasma/ 300 °C
- Trimetylborane (TMB)
- Post anneal 400 °C
- Yields 13 mol % B [Ref. 2]

B-graphene seeds

Synthesis:
Freeze drying graphene oxide (GO) and B_2O_3 prior to B-G formation.



BC_x CVD w/plasma

- *Triethylborane (TEB)*
- *Without plasma*
- *With 13.75 MHz remote source /300 ˚C*
- *Annealed at 400 ˚C*

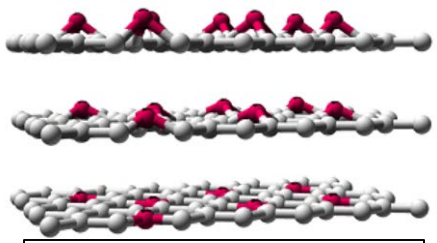
BC_x CVD w/o plasma

- Pyrolysis *800- 1000 ˚C*
- Triethylborane (TEB)

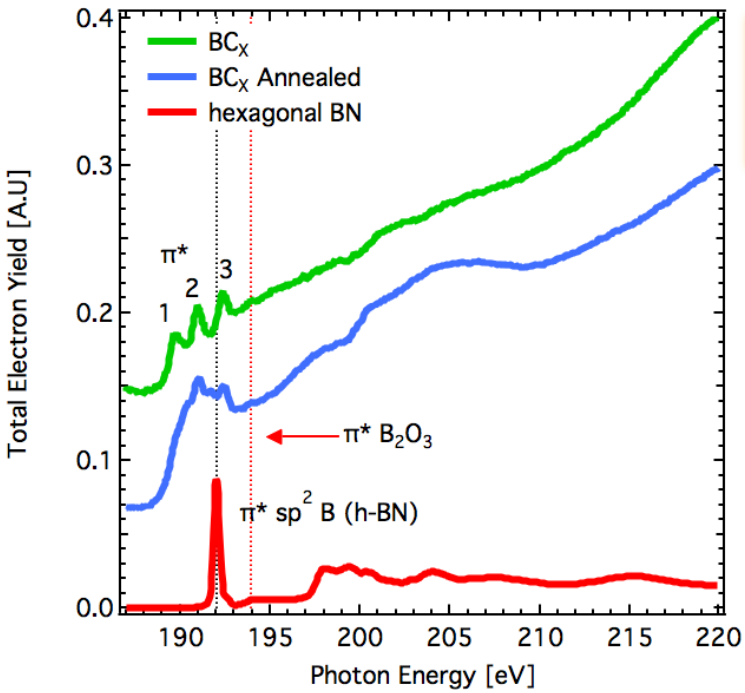
Accomplishments: Improve isosteric ΔH_{ads} for carbon sorbents with B- and N- incorporation

Increasing the isosteric ΔH_{Ads} for H_2 is predicted to occur via B and N substitution into graphitic carbon.

- Synthesize: $(B,N)C_x$ where B '*pucker*' from sp^2-like C
- Achieve physisorption B.E. = 10-15 kJ/mol H_2 on carbon sorbents



$(B,N)C_X$ graphitic puckering



NEXAFS data for BCx compared to h-BN

Boron adopts a mixture sp^2 and disrupted-sp^2 consistent w/puckering.

NEXAFS of the B 1*s* absorption edge indicate boron structure:

- π* 1: B-C phase 1
- π* 2: B-C phase 2 } *Non-planar/puckering*
- π* 3: hexagonal BN sp^2 B
- No boron-oxygen

Estimated 5 mol % B via XPS

Method: *BC_X via CVD on B-graphene 'seeds'.*

1. B_2O_3 and graphene oxide annealed at ≥1000 °C yields B-graphene seeds
2. Plasma CVD with triethyborane on B-graphene seeds

Accomplishment: Preliminary TPD Data, B- and N-Doped

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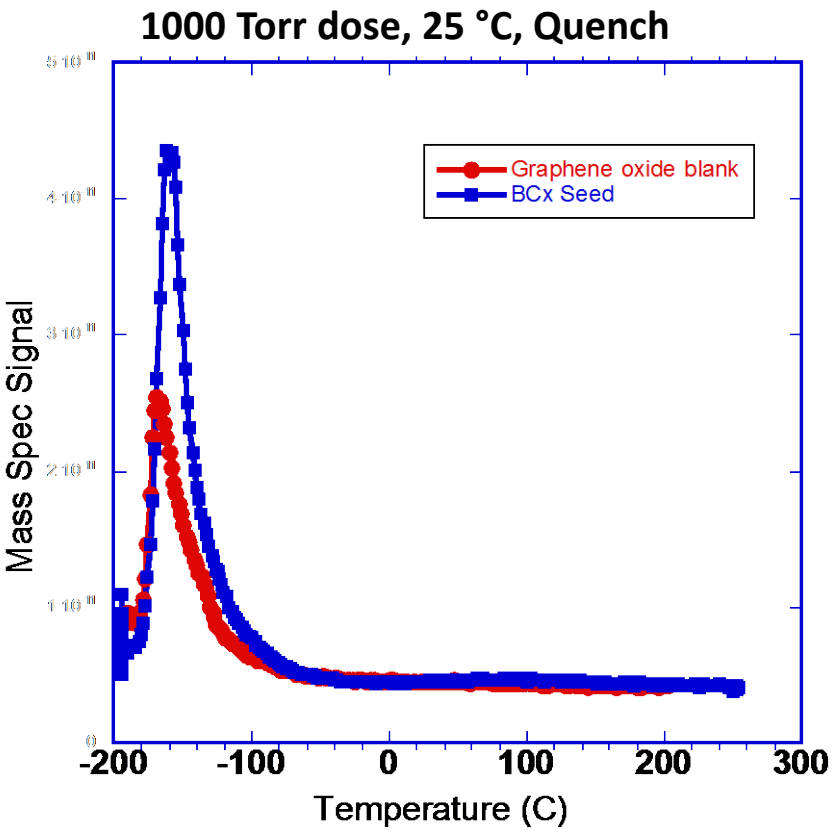
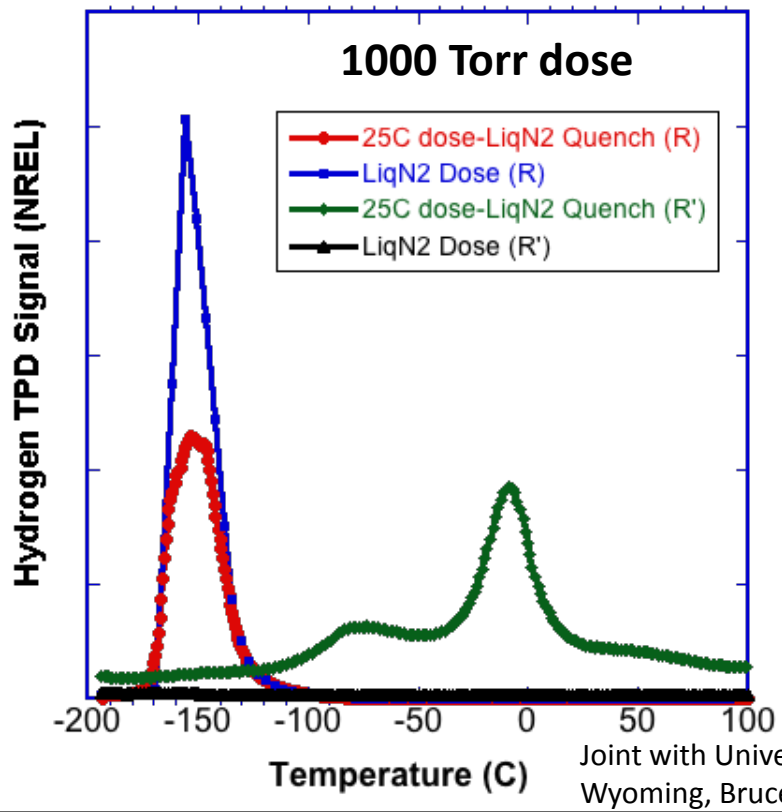
- **BCx data**

Nanoporous nitrogen matrix material,
Disordered framework C_2N species no metal
ΔH_{ads} = -25kj/mole for O °C peak
Altering R groups to enhance capacity





Joint with University of Wyoming, Bruce Parkinson

Collaboration: Selected Highlights

HySCORE – HyMARC Collaborations

- Materials Characterizations
  - ^{11}B NMR, PCT, TPD, DRIFTS, QENS, High pressure PCT (>350 bar), Thermal Conductivity, Neutron Spin-Echo, Synthetic approaches.
- Benchmarking Theory for Sorbents and Hydrides
  - Several joint journal articles published (3) and under development (5)
- Multiple Site visits
- Weekly Conference Calls (PNNL-NREL-LLNL), Monthly HyMARC-HySCORE-DOE

International: IEA-HIA Task 32

- NREL, NIST, PNNL all attended IEA meetings over past year (Japan, Korea, Berlin, Boston, Hawaii).

HySCORE Selected Highlights

- Established a consensus with DOE, Tech Team and several International partners for protocols that standardize measurement and reporting of hydrogen storage performance metrics for sorbent materials. (*Appl. Phys. A* 2016, *122*, 42; *Appl. Phys. A* 2016, *122*, 201)
- Observed and verified the binding of two hydrogen molecules to an unsaturated metal center within a metal organic framework material. (*Chem. Commun.* 2016, *52*, 8251-8254.)
- Predicted enhancement of hydrogen binding energies for metal-catecholate sorbent matrices. Experimentally validated that the hydrogen desorption temperatures in model metal-catecholate sorbent matrices can be "controlled" by altering the metal centers (80 to 350K).
- Enhanced the kinetics of hydrogen interaction with borohydride materials. Validated that key additives increase rate and reduce the temperature of H_2 uptake and release through a new mechanism. (Tom Autrey ST-132)
- Theory/Experiment collaboration within HySCORE to determine the effect of B and/or N doping on the isosteric heats of adsorption in sorbents.
- 20+ publications, 40+ presentations, 3 presentation awards

Remaining Challenges and Barriers

HySCORE

- **Ability to measure both anisotropic and isotropic thermal conductivity in advanced framework and carbon based sorbents.**
  - Difficult over the range of pressures and temperatures, developing new protocols
- **Ability to accurately define the isothermal region within the new variable temperature PCT system and validate performance at various temperatures.**
  - New protocols under development
- **Ability to define and control the relationship between the kinetic and thermodynamic effects within the catechol and B-N materials matrices as we move to more advanced self-assembled systems.**
  - Theory/Experiment collaborations
  - Effect of the extent of functionalization and metal type on capacity, number of hydrogen per metal centers, desorption temperatures and isosteric heats
    - Frameworks and sorbents
- **Ability to maximize the usable hydrogen for delivery to the fuel cell with high capacity materials.**
  - Altering the isosteric heats of adsorption by functionalization

Future Work: Materials

HySCORE

- **Materials**
  - Synthesize large batch PEEK-Cat-M samples for PCT/Neutron analysis
    - Determine the catechol level of functionalization on PEEK
    - Determine where hydrogen is adsorbing
  - BC_x seed materials
    - Determine the hetero-atom content
      - sp^2 vs sp^3 boron
    - Determine isosteric heats of adsorption
  - Carbon - Nitrogen rich framework materials
    - Ordered and disordered materials with different pore chemistries
  - Isosteric heats of adsorption
    - Determine the effect of metal centers the ΔH_{ads}

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

FY17 NREL Milestones

HySCORE

Description	Due	Status
Submit full report to DOE on results of volumetric capacity of at least 5-laboratory inter-lab comparison.	12/31/16	100% complete
Submit DOE report and/or a manuscript to peer-reviewed journal on Variable-Temperature Thermal Conductivity apparatus, methodology and results.	03/31/17	In progress, delayed due to staff departure and DOE request for additional experiments.
Completed construction of variable-temperature cyro-cooling add-on to the PCT Apparatus. Perform validated gravimetric capacity, volumetric capacity and isosteric heats of adsorption determination on an agreed upon sorbent standard to within 15% of the accepted value.	06/30/17	In progress and on schedule.
Measure and validate the gravimetric capacity, volumetric capacity and/or thermal conductivity of 2 samples as assigned by DOE. Submit full report to DOE within 30 days of completion of analysis.	09/30/17	In progress and on schedule. 1st sample measured and reported on. 2nd sample awaiting DOE request.

FY17 HySCORE Milestones

Description	Due	Status
Demonstrate H_2 addition to solid-state triazine at temperatures < 100 C and pressure < 50 bar.	12/31/16	100% complete
Synthesize a framework, aerogel or polymeric material exhibiting a total H_2 storage capacity of at least 30 g/L at temperatures above 100 K and < 150 bar.	03/31/17	In progress, delayed due safety testing at NREL of new VTPCT temperature sample holder for verification. Sample synthesized.
Demonstrate computational accuracy by showing that the calculated capacity for a MOF, PAF, or carbon-based material with multiple H_2 molecules bound per metal is within 15% of the experimental capacity	06/30/17	In progress and on schedule.

FY17 HySCORE Milestones

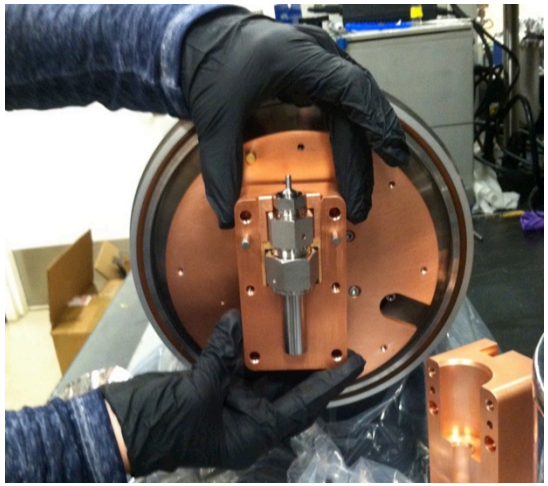
Description	Due	Status
Go/No-Gos: 1. Triazine-based hydrogen carriers: Solid phase organic carrier: if > 50g H2/L uptake is observed in solid phase triazine at T < 100 C and P < 100 bar, then go. If <50 g H2/L then no-go on solid phase organic carriers: Liquid phase organic carriers: if blend of perhydrotriazines are liquid at room temperature and remain liquid after H2 release and release > 48g H2/L at T < 100 C and P < 100 bar, then go, otherwise no-go. If carriers or spent fuel are solid then no go on liquid carriers. *2. Determine the viability of Boron and nitrogen doped materials for increased binding energy and capacities that could approach 2020 goal* *a. Demonstrate reversible hydrogen uptake within a molecular solid-FLPs, sorption <30 minutes at 25 °C and desorption <60 minutes at 120 °C.* *b. Synthesize a boron or nitrogen or co-doped sorbent with >8 atomic percent dopant incorporated into the backbone, with 2000 m^2/gram surface area and a hydrogen binding energy >12 kj/mole.*	09/30/17	In progress, on track

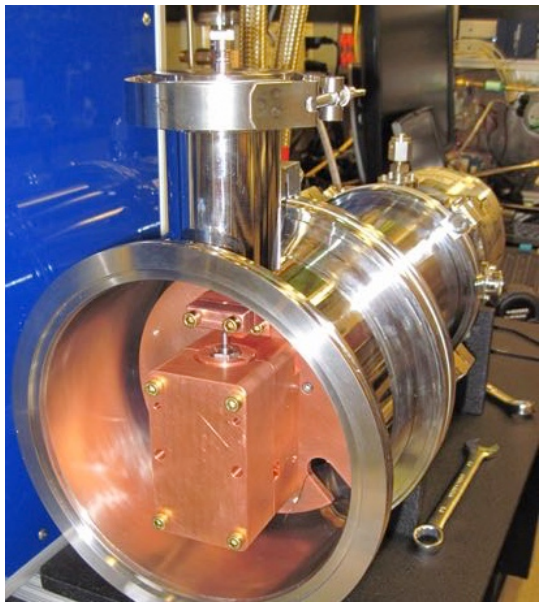
Acknowledgements

We acknowledge research support from the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, under Contract No. DE-AC36-08-GO28308

Technical Back-up slides

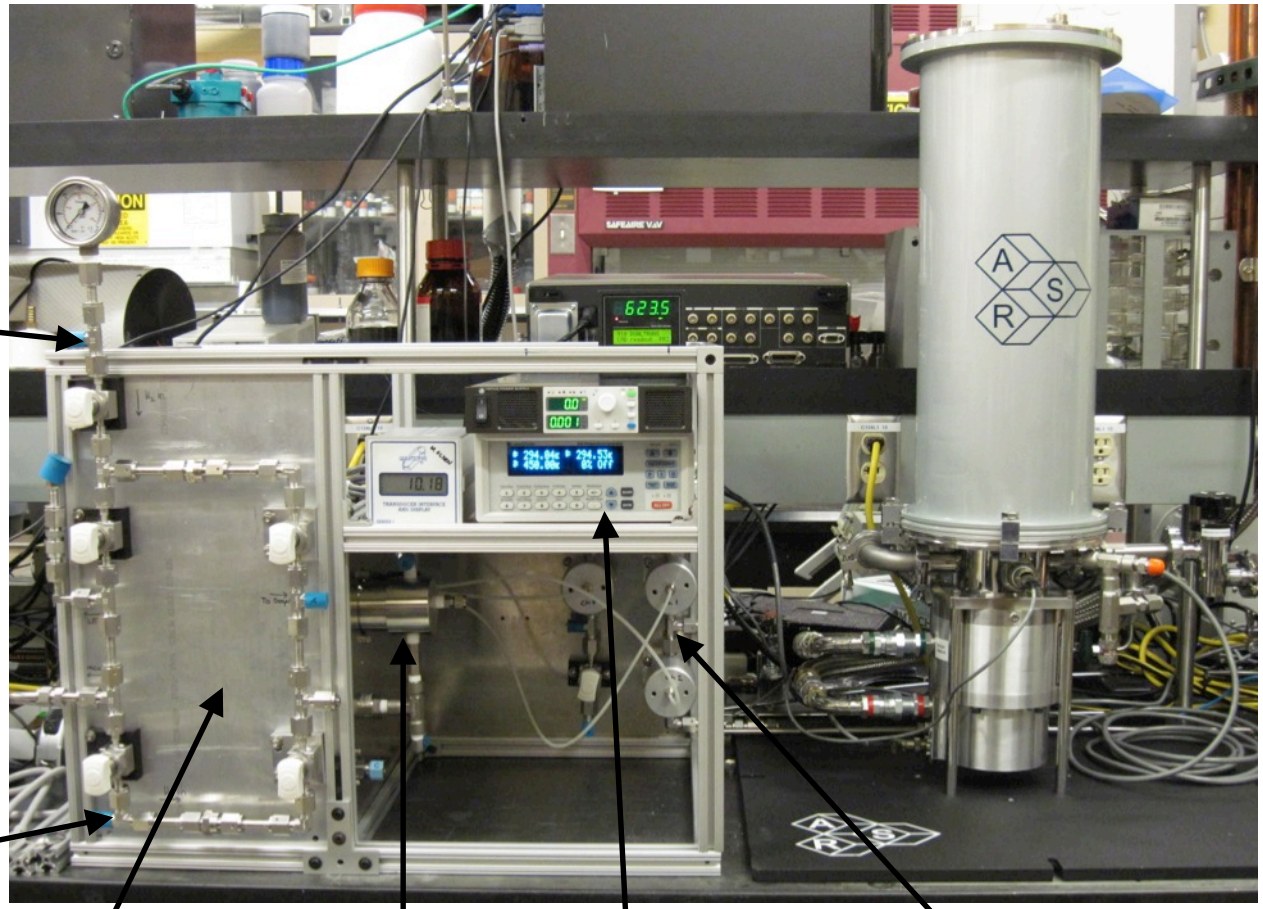
Accomplishment: Continuously Variable Temperature PCT





- **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

Accomplishments:
TC Cryostat and pressure-control system



Major Goals

HySCORE

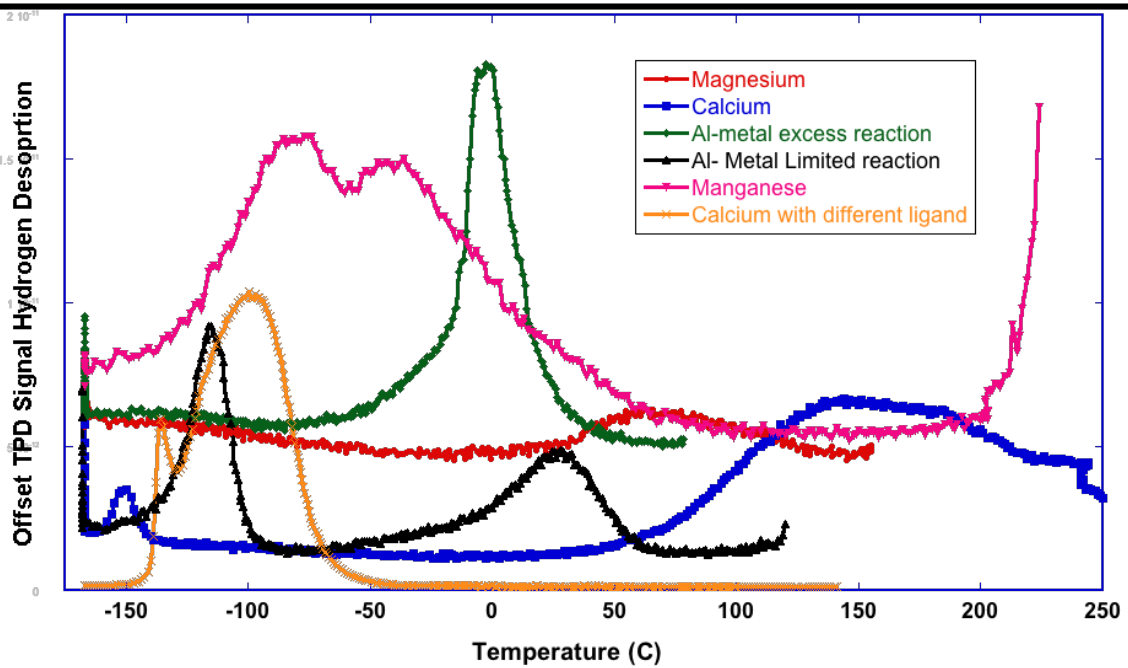
Near Term: (FY 17 milestone driven)

- **Advance Core Capabilities:**
  - Neutron spin-echo (NSE); Variable temperature PCT; *in-situ* DRIFTS measurement
  - Publish definitive article on the round-robin results for further acceptance of protocols
- **Advance Materials Performance**
  - Improve capacity of new multiple hydrogen metal-center materials and metal-catecholate sorbents.
  - Determine the viability of boron and nitrogen doped 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.

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.**
- Establish if/how additives necessary modify the properties of H_2 storage materials

Accomplishment: Effect of Metal on Desorption Temperature (FY 16)



Demonstrated the ability to alter the hydrogen desorption temperature

Will now work to improve capacity.

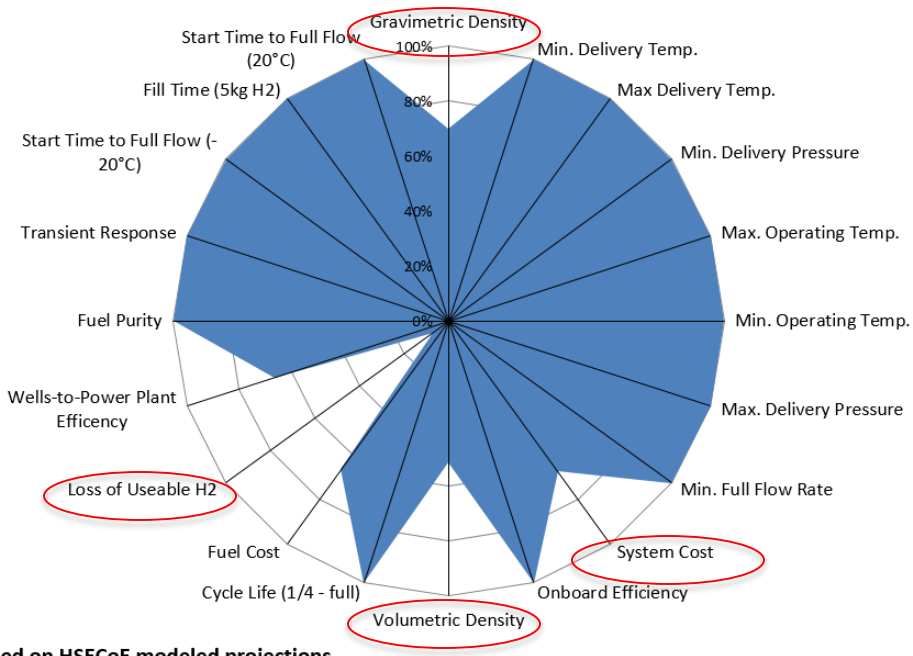
Metal/Ligand	Desorption Temperature (K)	Gravimetric capacity (1 bar) %w/w approximate
Be/mixed oxalate	150 K	<0.2%
Al/mixed oxalate	125 - 175 K (small pk 273K)	0.1 – 0.3%
Ca/mixed oxalate	150 – 225K	0.4 – 0.8%
Mg/croconate	340K	< 0.1%
Ca/Croconate	350 – 473 K	< 0.1%
Al/Croconate (a)	265 – 290 K	0.5 –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

Hydrogen Storage Engineering Center of Excellence: Sorbents

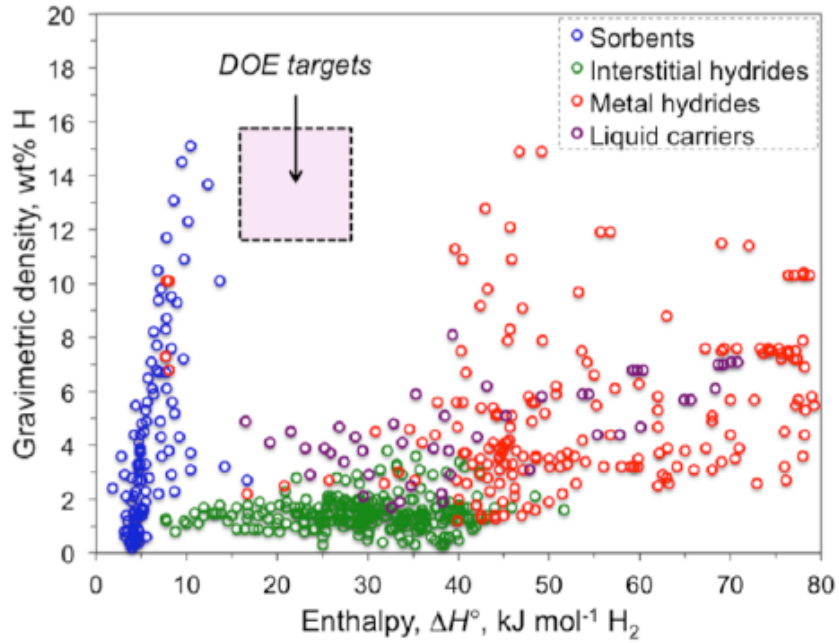
Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Projected MOF-5 System Compared Against 2020 Targets

(100 bar, 80-160K, Type I Tank, Hexcell - loose powder)

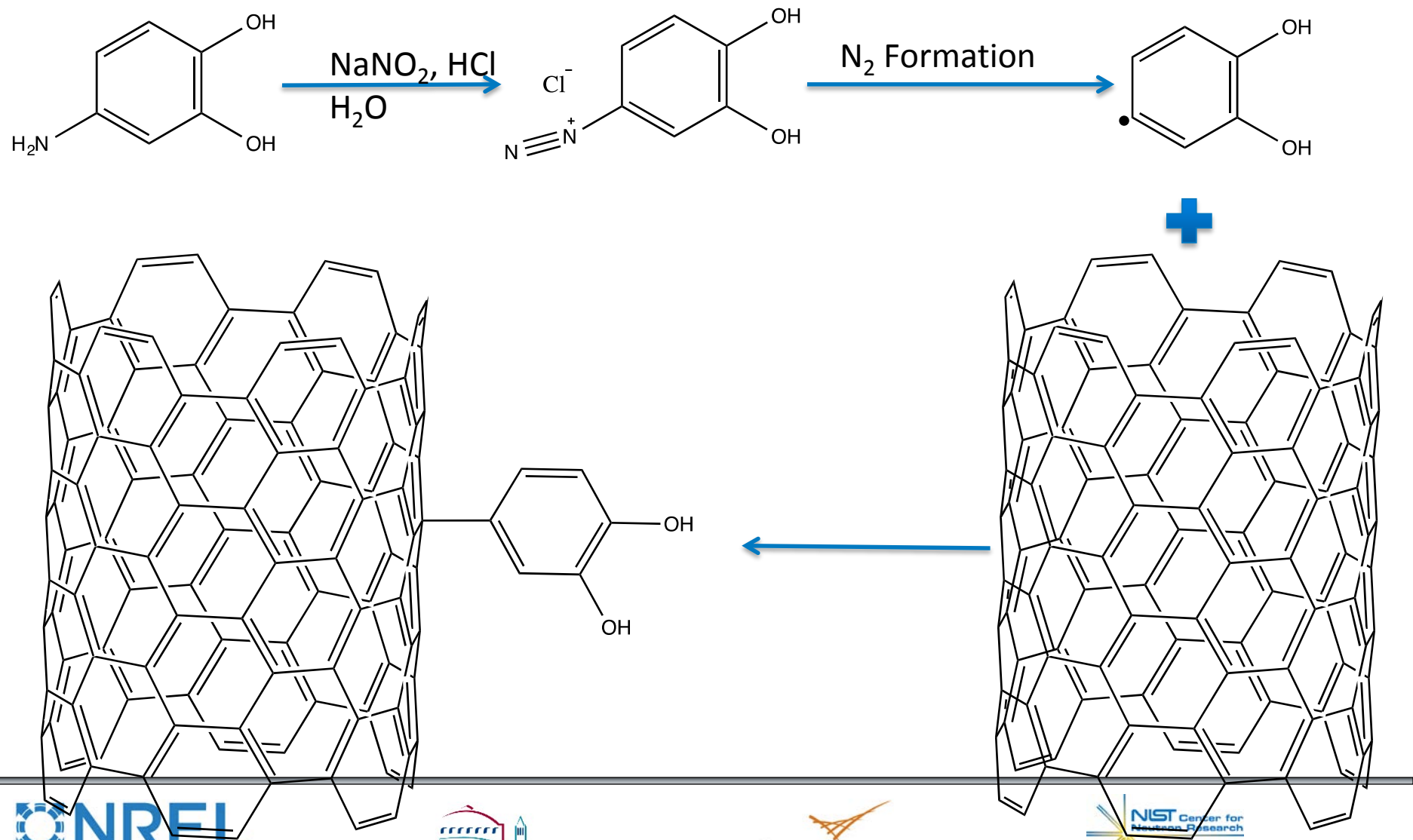


Status based on HSECoE modeled projections

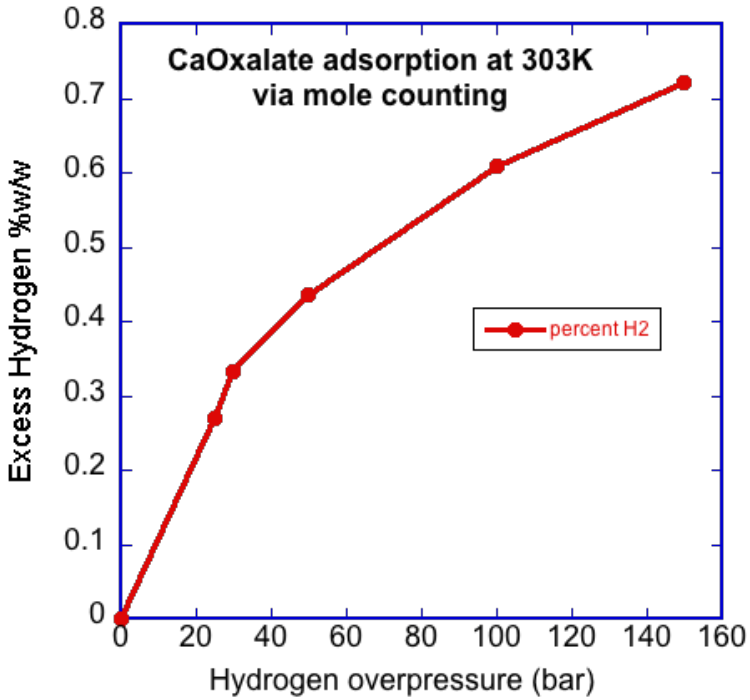


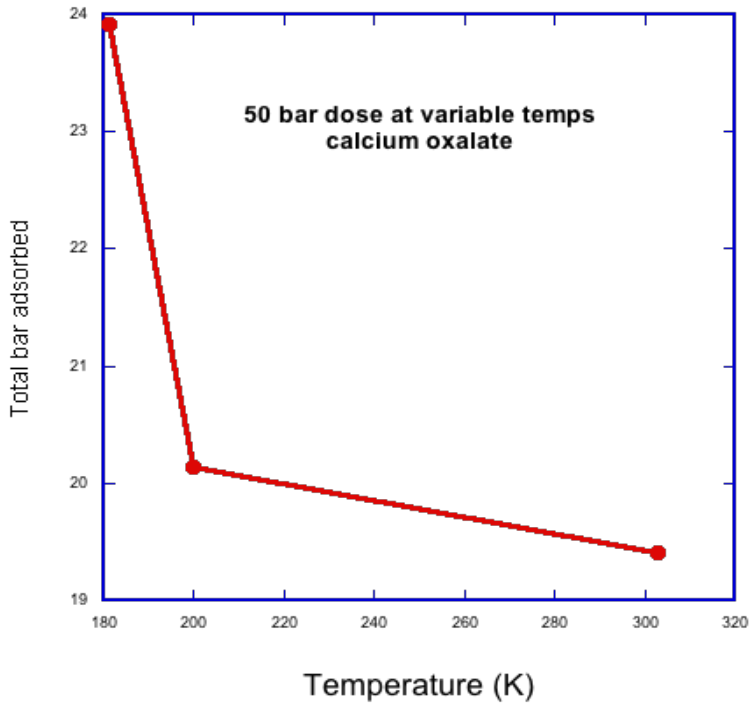
Source: DOE Hydrogen Storage Materials Database

Accomplishments: Diazonium coupling



Mole Counting Experiment

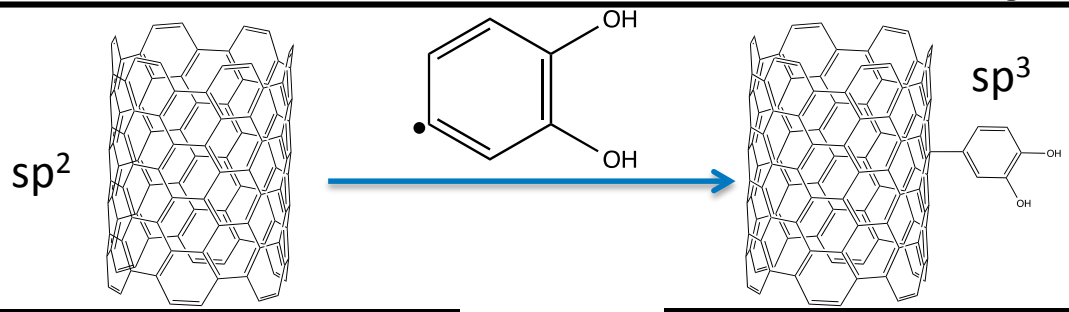


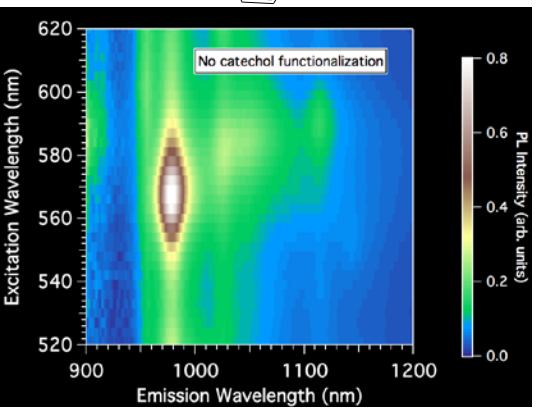


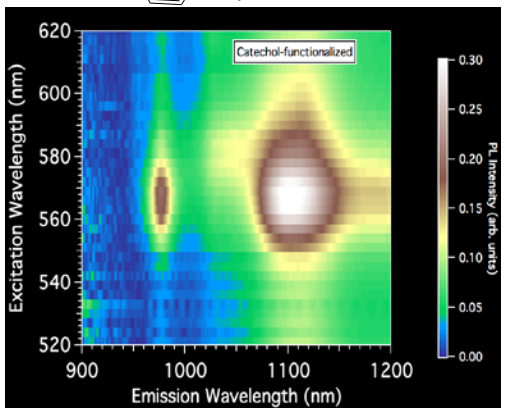
Room Temperature dose with 77K quench gives 0.75% w/w H_2
180K dose with 77K quench results in 1.2%w/w H_2

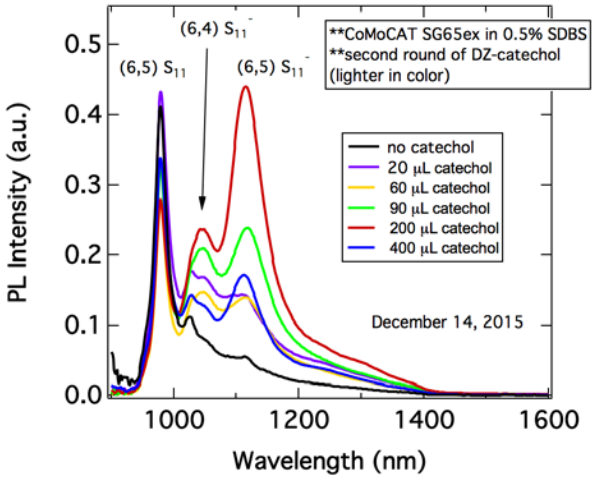
At 77K there is zero adsorption after 6 hrs.

Accomplishment: Modified sorbent pore structure/chemistry









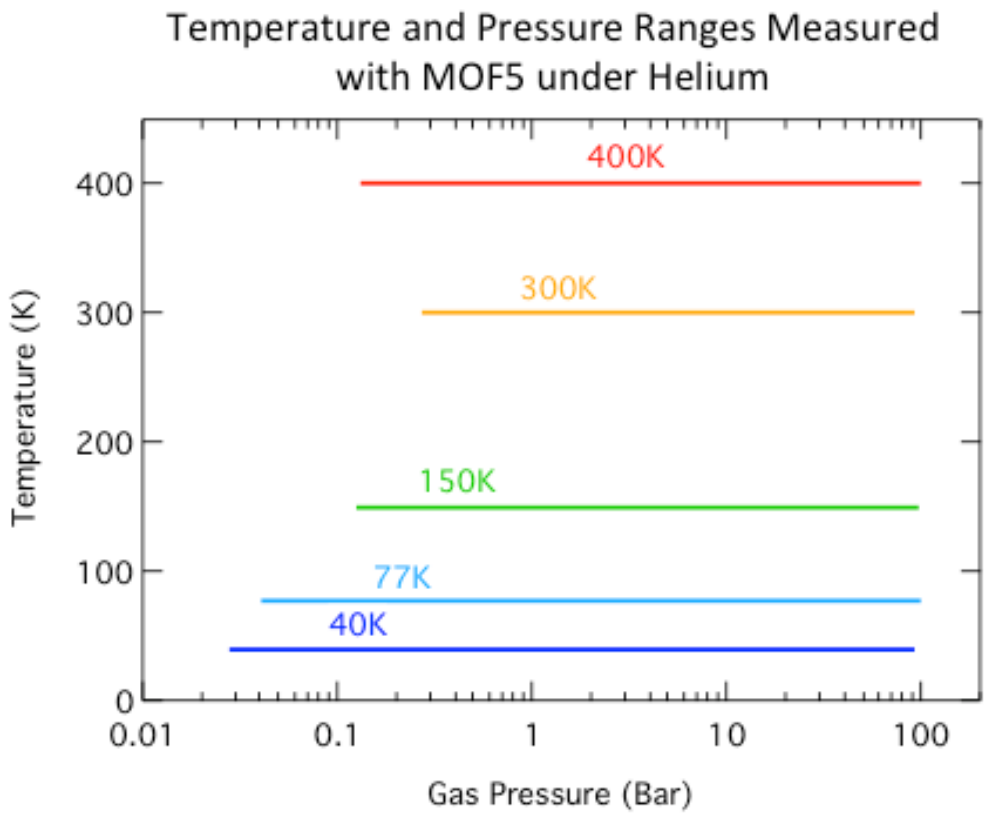
PL dominated by emission at 990nm from sp^2 for pristine SWCNTs

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.

TC Working Range

Tests Over Full Range of Temperature and Pressure

Using MOF-5 samples in helium, measurements were made at 5 selected temperatures and >10 pressures, spanning the full range of the instrument's capabilities.

Measured thermal conductivity values range from 0.1 to 0.3 W/(m K).