NREL HyMARC Technical Activities

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National Renewable Energy Laboratory

May 1, 2019

DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

ST131

Overview

Timeline*

Phase 1: 10/1/2015 to 9/30/2018
Phase 2: 10/1/2018 to 9/30/2022
Project continuation determined annually by DOE.
(*previously a component of NREL's materials development program and supported annually since 2006)

Budget

NREL:
FY 18 HyMARC Phase 1 - $450k
FY 18 HyMARC Phase 2 - $1.2M
FY 19 HyMARC Phase 2 - $450k**

Note: includes $ for DataHub;
postdocs at NIST and SLAC

**funds received as of 3/31/19

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, Terrence Udovic
SLAC – Michael Toney
HyMARC – SNL, LLNL, LBNL, PNNL team members
H_2ST^2, USA – Hydrogen Storage Tech Team
Colorado School of Mines - Colin Wolden, Brian Trewyn, Alan Sellinger
Univ. Hawaii – Craig Jensen, Godwin Severa
Université de Genève – Hans-Rudolf Hagemann, Angelina Gigante

Relevance: NREL Role

- **Perform validation measurements for DOE**
- **Collaborate with other groups to characterize H_2 adsorption**
  - BET, TPD, PCT, DRIFTS, DSC/TGA, Raman, TC measurements
- **Promote hydrogen adsorption measurement accuracy**
  - Measurement/Reporting Protocols
  - Develop universal protocols for thermodynamic property calculations
- **Design and develop next generation hydrogen storage materials**
- **Advance hydrogen carriers research effort**
  - Seek/develop/advance new concepts and materials that have potential to provide advantages over conventional compressed and liquefied hydrogen for bulk storage and transport of hydrogen (H2@Scale)
- **Utilize new advanced characterization techniques**
  - Cryo-PCT system, Cryo-TC system, PCT-calorimetry, PCT-liquid carriers
  - *in-situ* capabilities through SLAC & NIST collaborations
- **Support seedling projects**
- **DataHub design and management**

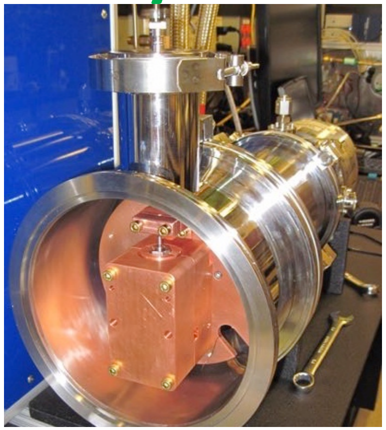
NREL Approach: Focus Areas: Black–active (AMR slides), Purple-active, Blue-future

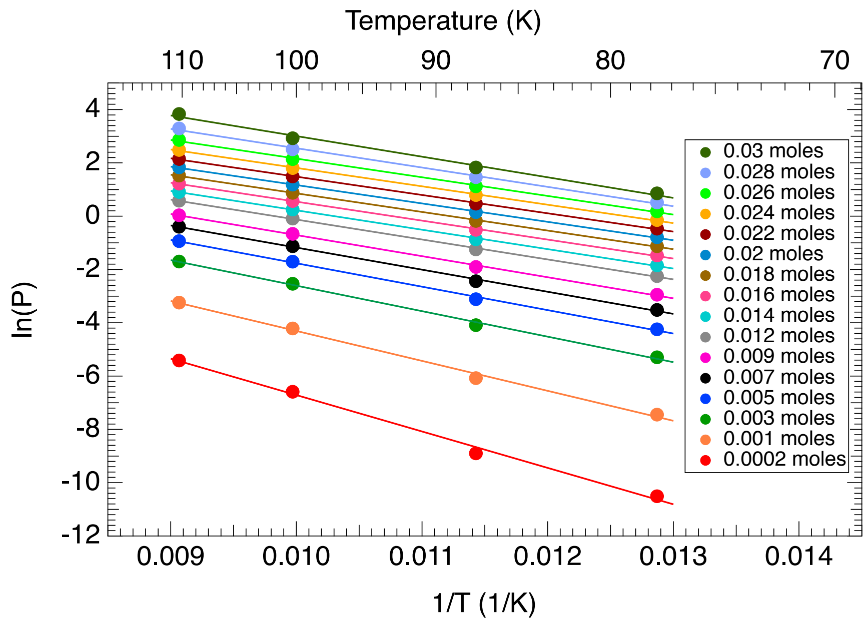
- **Task 1 Sorbents**
  - 1.A Focus Area: Enthalpy / Entropy and Isosteric Heat. (Q_{st})
  - 1.B Focus Area: Optimizing Sorbent Binding Energies (starts Q3-FY19)
  - 1.C Focus Area: Optimizing of Sorbent Packing (rev. only slide)
  - 1.D Dynamic Sorbent Materials (Starts Q4 FY19)
- **Task 2 Hydrides**
  - 2.A Focus Area: MH Thermodynamics
  - 2.C Focus Area: Activation of B-B and B-H Bonds
  - 2.D Focus Area: Nanoscaling to improve thermodynamics and kinetics
- **Task 3 Hydrogen Carriers**
  - 3.C Focus area: Liquid hydride systems as hydrogen carriers (eutectics, ionic liquids, etc) (rev. only slide)
  - 3.D Focus area: Investigation of adsorbents as hydrogen carriers. (Porous liquids)
  - 3.E Focus area: Bioinspired materials as hydrogen carriers (starts Q3-FY19)
  - 3.F Focus area: Plasmonic 'on-demand' hydrogen release in hydrogen carriers
  - 3.G Focus area: Heterolytic cleavage and activation of hydrogen (FLPs) (Starts Q4-FY19)
- **Task 4 Development of Advanced Characterization Core Capabilities**
  - 4.A Focus area: High temperature validated PCT system
  - 4.B Focus area: PCT calorimetry (start Q3-FY19)
  - 4.D Focus area: *in-situ* and *ex-situ* X-ray (SLAC), Neutron (NIST), Raman and DRIFTS characterization techniques
  - 3.B.4 Liquid Hydrogen Carrier Capacity Determination (Starts Q4-FY19)
- **Task 5: Research Support for HyMARC Seedling and Lab Call Initiatives**
  - 5.A. Validation, Characterization support
  - 5.C Support of DOE-FOA.
- **Task 6: HyMARC Data Hub (rev. only slide)**

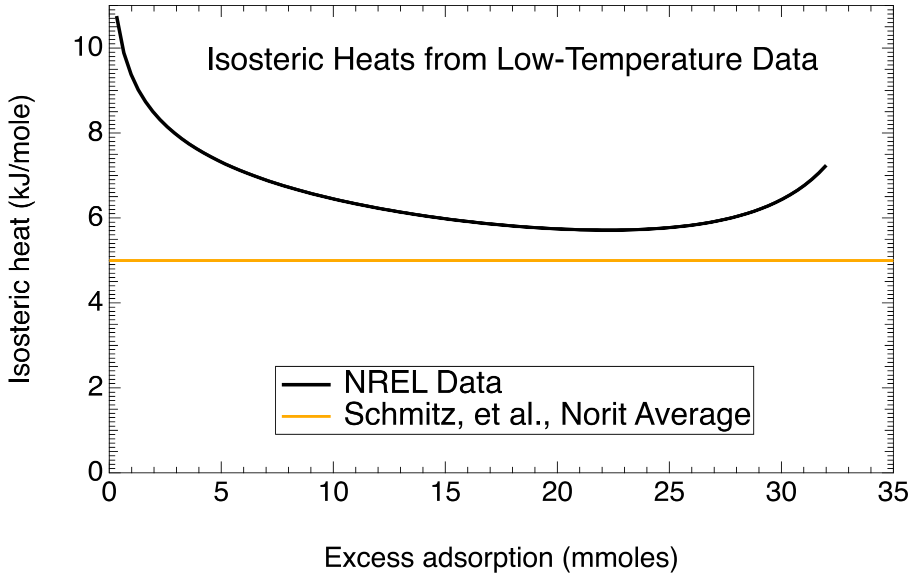
Accomplishment: Task 1a Enthalpy/Entropy and Isosteric Heat. (Q_{st})

PEMP Milestone completed: Isosteric heats with Cryo-PCT

- To test Cryo-PCT, determined Q_{st} of known material
- Good agreement with literature
- Several issues were realized that could influence Q_{st} determination







Accomplishment: Task 1a Enthalpy/Entropy and Isosteric Heat. (Q_{st})

Issues Investigated with Isosteric Heat Determination

- Experiment, Analysis, Interpretation
- Supercritical region especially problematic

Subcritical, Ideal Gas

$$\frac{\partial P}{\partial T} = \frac{Q_{st}}{T(\bar{v}_1 - \bar{v}_2)} \rightarrow Q_{st} = -R\left(\frac{\partial ln(P)}{\partial(\frac{1}{T})}\right)_n$$

Supercritical, Non-Ideal

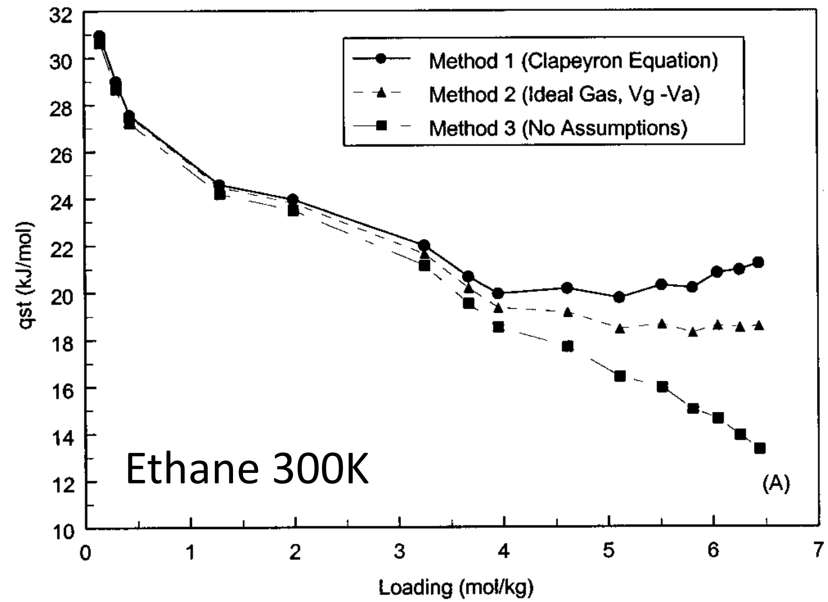
$$-R\, z(P,T)\, \frac{\partial(ln(P))}{\partial(\frac{1}{T})} = \frac{Q_{st}}{(1 - f(P,T))}$$

Examination of the Approximations Used in Determining the Isosteric Heat of Adsorption from the Clausius−Clapeyron Equation

Huanhua Pan, James A. Ritter, and Perla B. Balbuena*

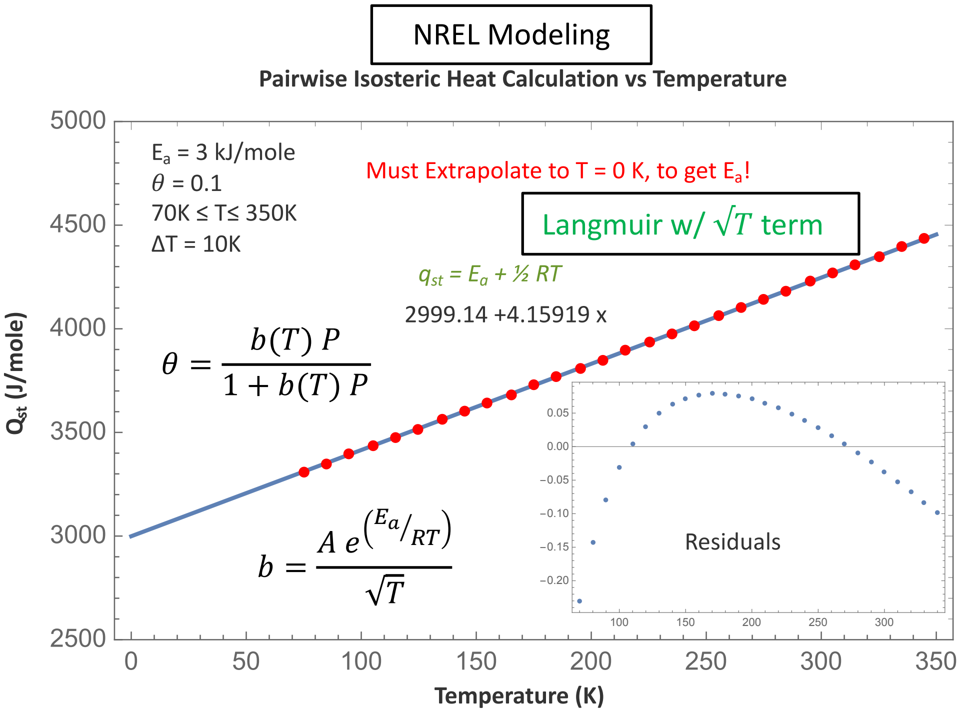
Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia, South Carolina 29208

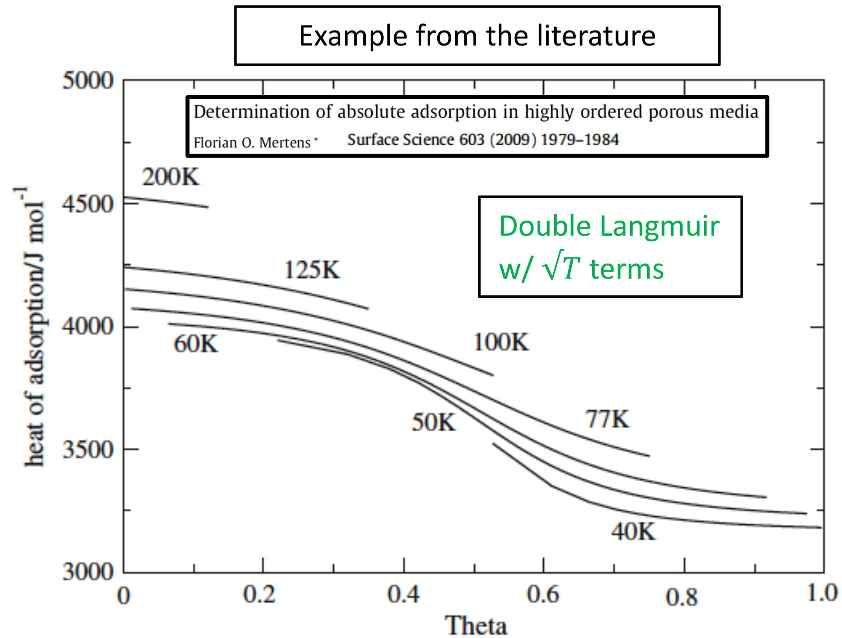
Langmuir **1998**, *14*, 6323−6327



Issues Investigated with Isosteric Heat Determination

- Approach: Sources of bias in Q_{st} explored using isotherm modeling
- Explicit T dependence in isotherms can introduce bias
- This can lead to mis-interpretation of the results





Issues Investigated with Isosteric Heat Determination

- Other issues that have been investigated or are being investigated:
  - Effect of isotherm calibration error on Q_{st}
  - Excess vs absolute isotherms and Q_{st}
  - Best way to fit isotherms for Q_{st} analysis to minimize error & bias
  - Understanding double Langmuir and its Q_{st} determination
- Future Work:
  - Changing Q_{st} calculation to include non-ideality
  - Further investigating supercritical issues for Q_{st}
  - How heterogenous sites effect Q_{st} and can optimize material
  - Validity of van't Hoff with respect to isotherm equations
  - Can a detailed equilibrium constant examination provide additional insight into adsorption mechanics?

Approach: Task 2c Activation of B-B and B-H Bonds

Relevance:

Facilitate H_2 adsorption in MgB_2 and $Mg(BH_4)_2$ systems

Approach:

Additives: Disrupt the Mg-B matrix by adding organics,

e.g. THF incorporation based on previous HyMARC work[1-3]

Uniqueness of this project:

- Vapor phase transport of THF to control the amount of THF incorporated.
- Attempt to vary/control the pathway of THF "incorporation" as compared to ball milling.

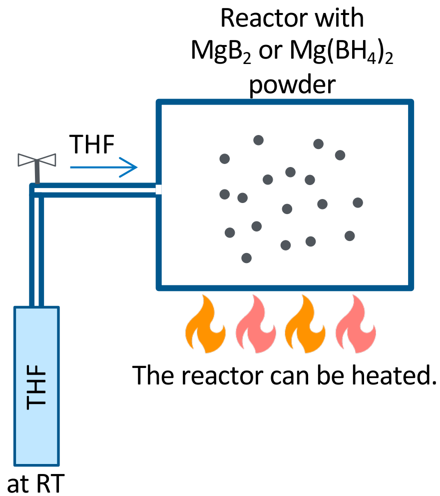
[1] Severa *et al.*, ChemPhysChem 2019, 20, 1–5 (HyMARC)

[2] Severa *et al.*, *Chem. Commun.*, **46**, 421–423 (2010)

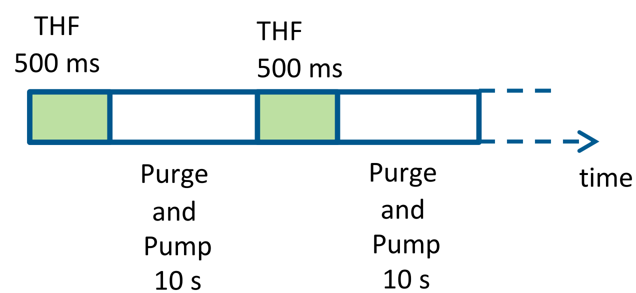
[3] PNNL: Chong *et al.*, *Inorganics*, **5**, 89 (2017)

Experimental:

Setup



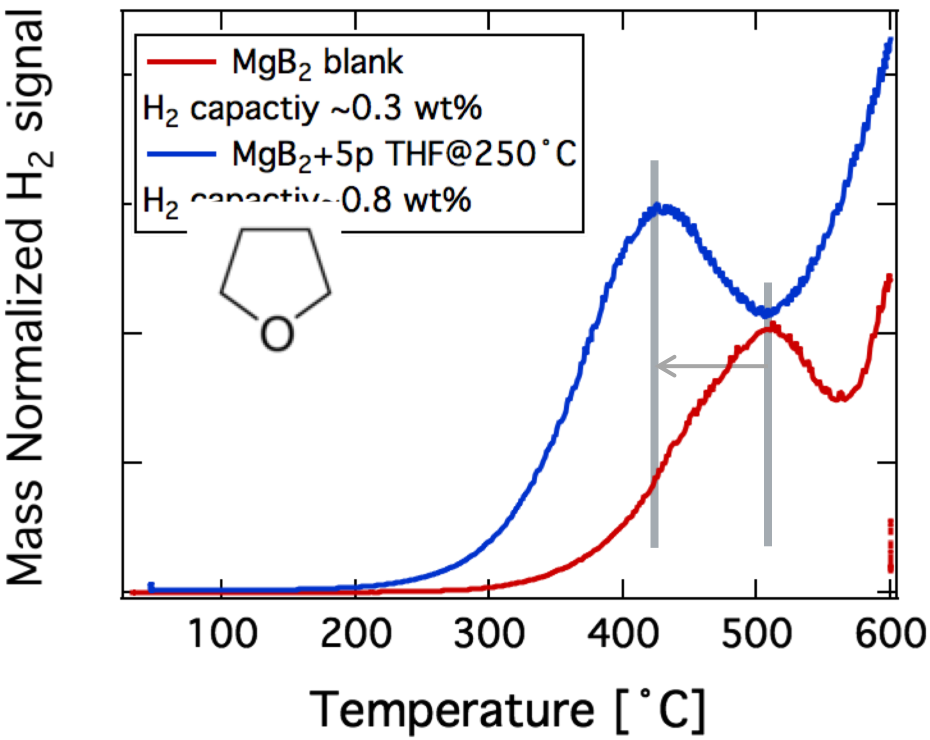
Pulse Sequence



Accomplishment: Task 2c Activation of B-B and B-H Bonds

MgB_2+THF results for H_2 absorption

Thermal Programmed Desorption



Initial results from the PCT at 250 ˚C

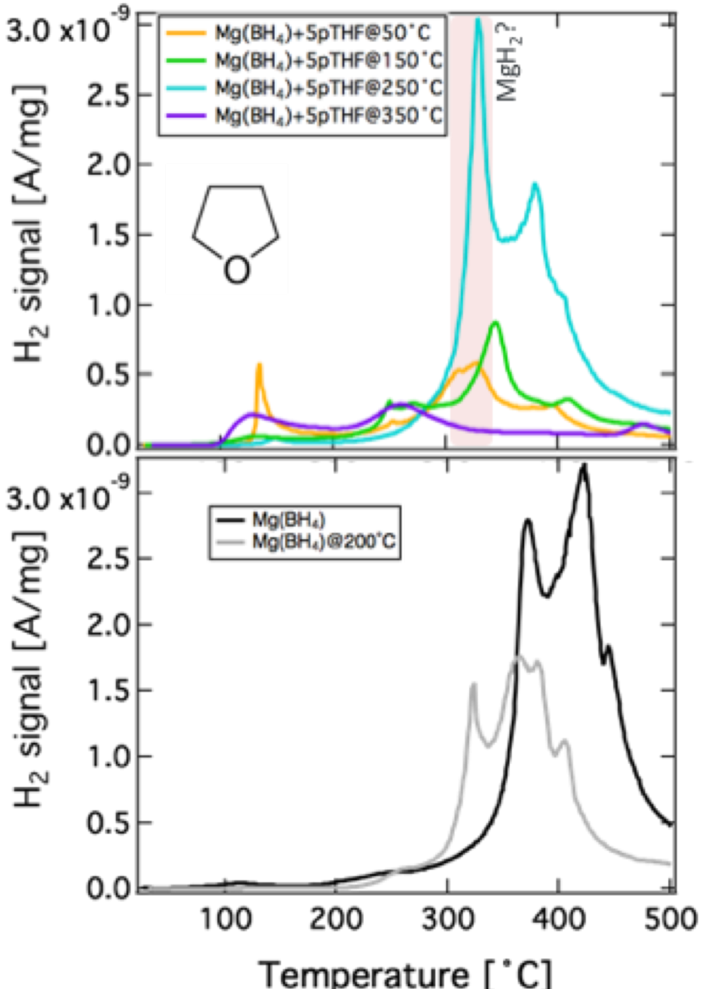
Sample	MgB2 + 25 p THF @ 350 °C	MgB2- Neat
Mass (mg)	134	329
Degas Temp (˚C)	250	250
Dosing Temp (˚C)	250	250
Time (hrs)	50	48
Nominal Pressure (bar)	120	127
Total ΔP (bar)	0.570	0.678
H_2 adsorbed (mmol)	0.170	0.202
H_2 adsorbed (mg)	0.339	0.403
Wt %	0.25±0.05%	0.12±0.02%

<u>Initial results suggest:</u>

- ➢ Increase in H_2 capacity compared to blank MgB_2 by ~2x
- ➢ Decrease of H_2 desorption temperature compared to blank MgB_2 by ~80˚C

Accomplishment: Task 2c Activation of B-B and B-H Bonds

$Mg(BH_4)_2$+THF H_2 desorption

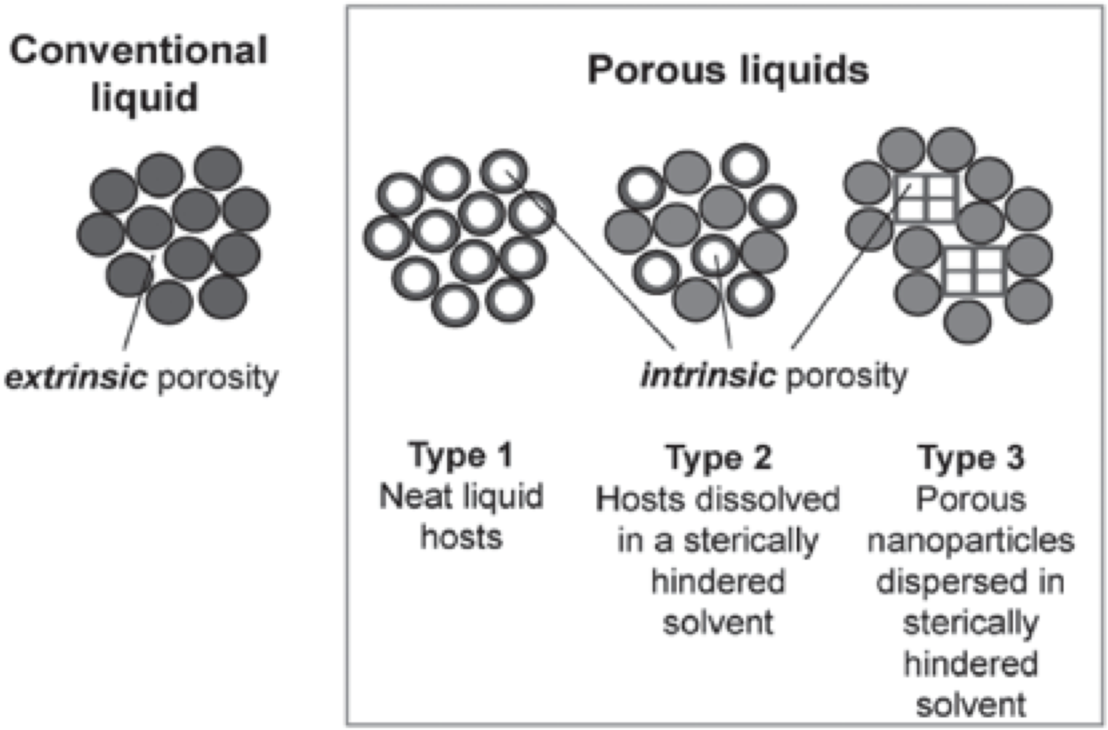


<u>Initial results suggest:</u>

- The THF treatment at 250˚C has an intense and sharply defined desorption peak at T~320˚C with a secondary peak at T~380˚C.
- Decrease of H_2 desorption temperature compared to blank (by ~60˚C). This is probably mainly due to the heat treatment only.
- Low temperature peak at ~300˚C correlates with formation of β- $Mg(BH_4)_2$.
- The intensity of this peak, however, hints to a different THF-induced H_2 desorption pathway. Note: Only negligible amounts of THF evolve at ~130˚C.

Relevance: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

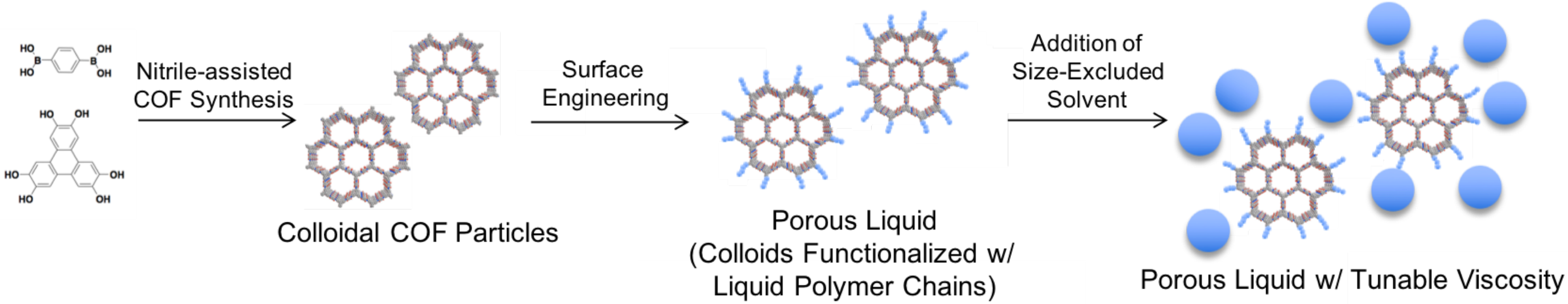
Conventional liquids only have extrinsic porosity, i.e., small transient and ill-defined pores, while the three types of porous liquids have intrinsic permanent porosity.



Benefits:

- **Decreased sorbent packing penalties**
- **Degrees of freedom increased**
- **Liquid transport options**
- **No solvent contaminants if type 1**
- **2 %w/w material with density of 1g/ml could deliver 500kg H_2. (current tech is 250 kg $H_{2(g)}$)**

Approach: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

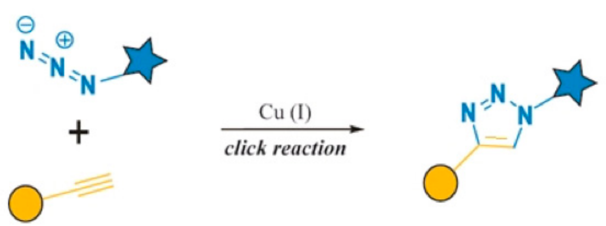


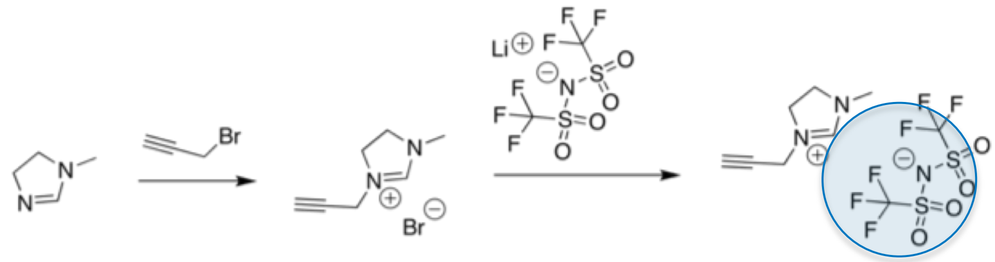
- COFs could provide unparalleled fine-tuning of gas selectivity/separation in porous liquids
- Consideration to (1) COF particle size, (2) COF pore size & co-solvent, (3) Functionalization
- Functionalization strategies: click chemistry of liquid polymer chains and/or tethered ILs

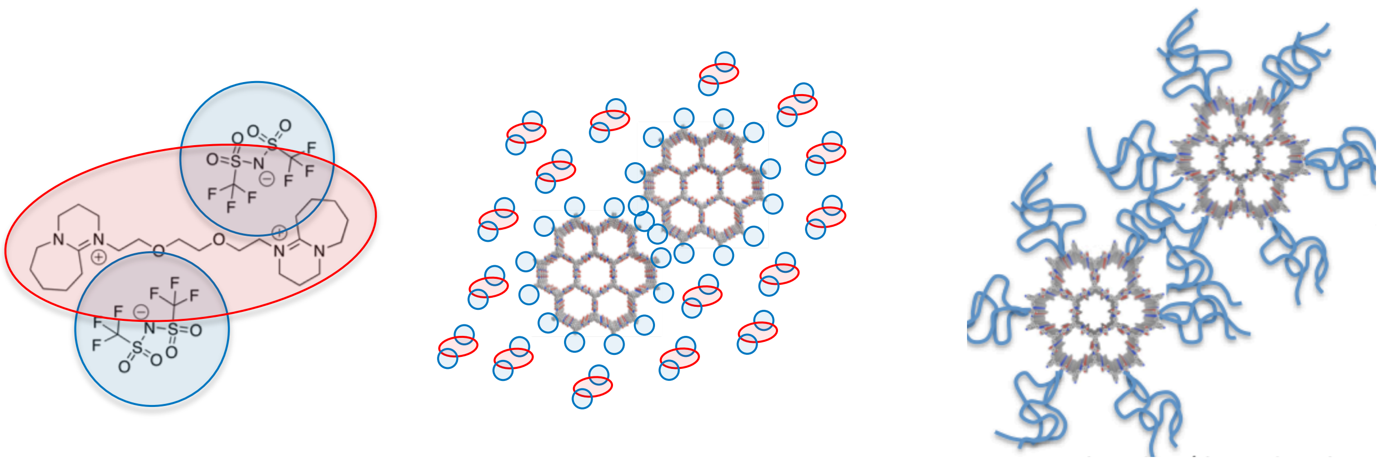
Approach: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

Click Chemistry Functionalization of COF

"Click" Chemistry

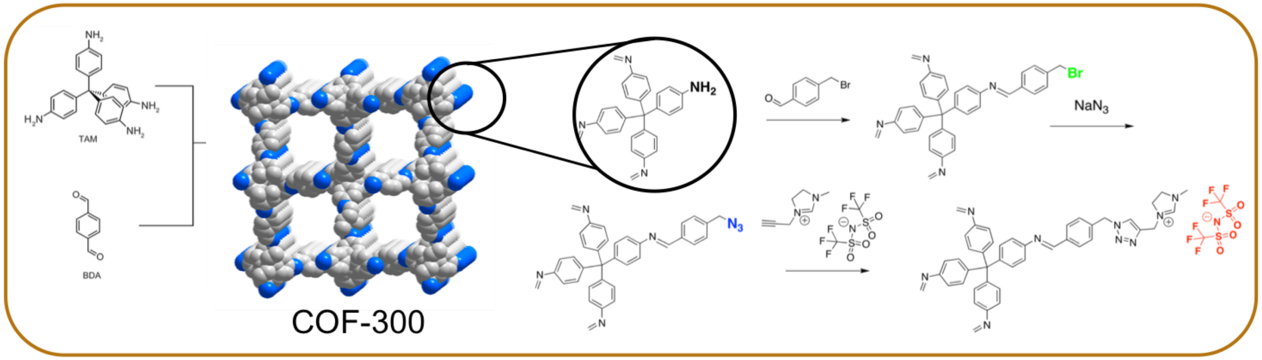


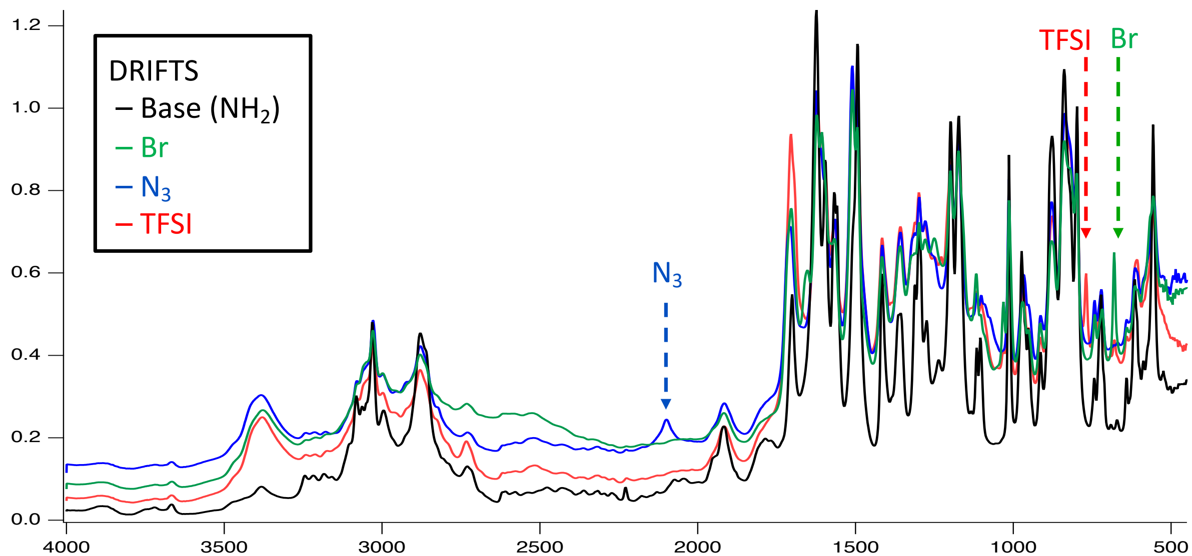




Accomplishment: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

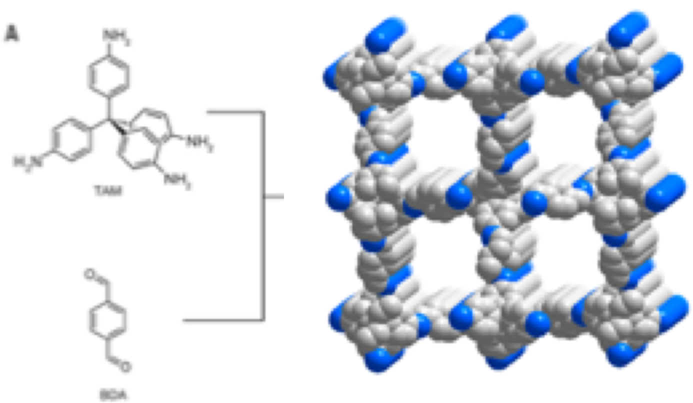
Confirmation of Click-Chemistry Reaction



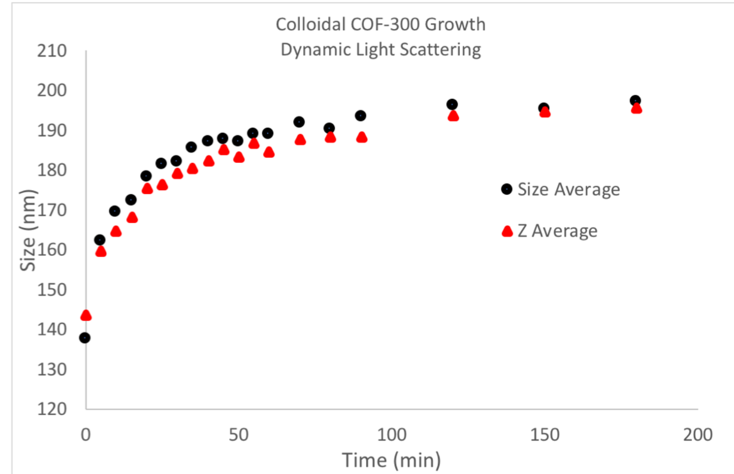


- DRIFTS results support that the click-chemistry synthesis was successful.
- Broadening of amine N-H stretch indicates chemical interaction.
- N_3 and C-Br stretches are only present in the relevant samples.
- New peaks (dashed lines) formed with the addition of TFSI are attributable to TFSI.
- **MILESTONE achieved**

Accomplishment: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)



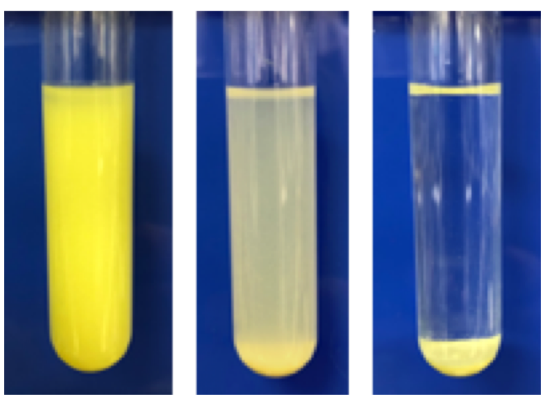
COF-300



Traditional Synthesis > 10 μm particles

Colloidal Synthesis, DLS vs time data

Suspension in CH_3CN

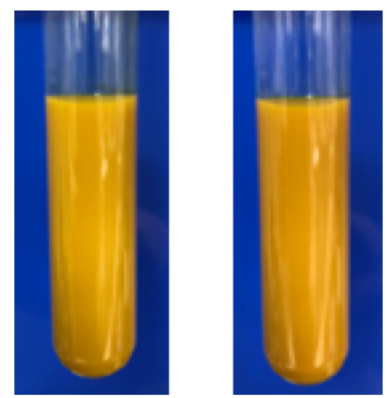


T_0 *1 h* *24 h*

Successful synthesis of small particles and colloidal suspension

TPD and "frozen" PCT are underway

Suspension in CH_3CN



T_0 *1 week*

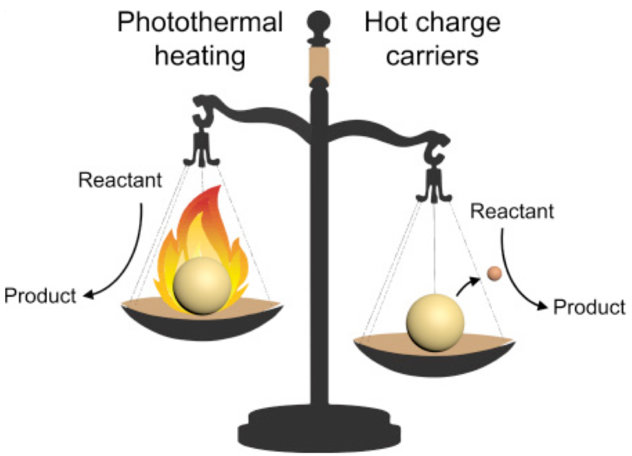
< 200 nm

Relevance: Task 3 Plasmonic 'on-demand' hydrogen release in hydrogen carriers

Plasmonic nanostructures concentrate photon energy and can produce heat via the localized surface plasmon resonance (LSPR)

- plasmonic nanostructures act to locally and temporally heat a limited region
- LSPR and its local intensity is determined by the material shape, size and crystallinity

Plasmonic Hot Carriers - using low-energy photons, generate high energy electrons and holes

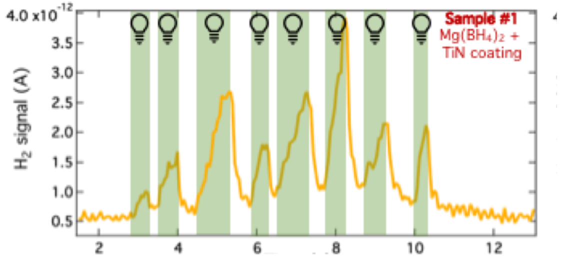


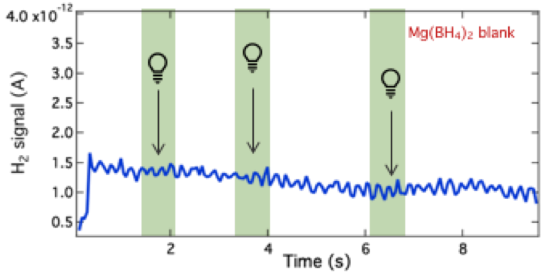
Utilize low energy light source to induce hydrogen sorption/desorption reactions and phase changes thermally and/or electrochemically

Pix from: https://www.differ.nl/vacancies/internship-nea

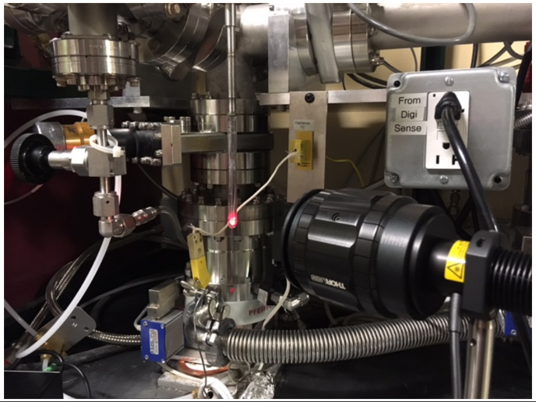
Accomplishment: Plasmonic 'on-demand' hydrogen release in hydrogen carriers

Hydrogen Desorption using Photons – $Mg(BH_4)_2$ and MgH_2





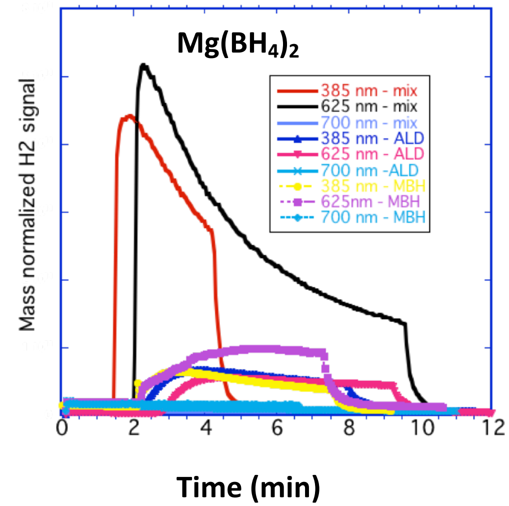
LEDs: 385 nm, 625 nm, 700 nm

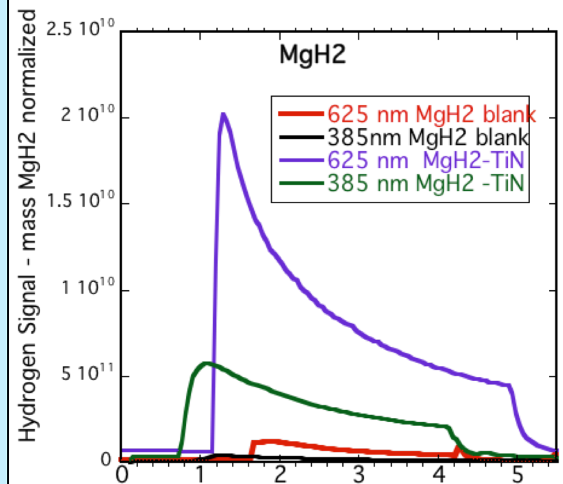


Mix: 20 nm TiN with $Mg(BH_4)_2$ or MgH_2
ALD: Atomic layer deposition of TiN on $Mg(BH_4)_2$
MBH: $Mg(BH_4)_2$

- **700 nm no hydrogen evolution**
- **625 nm (plasmonic heating) only H_2 and B_2H_6 observed**
- **385 nm (hot carrier) H_2, B_2H_6 and possibly B_3H_8, and B_2H_7 observed**

Preliminary Indications:
Non-optimized
625 nm – thermal degradation
385 nm – electrochemical reaction
Dual illumination and *in-situ* studies underway

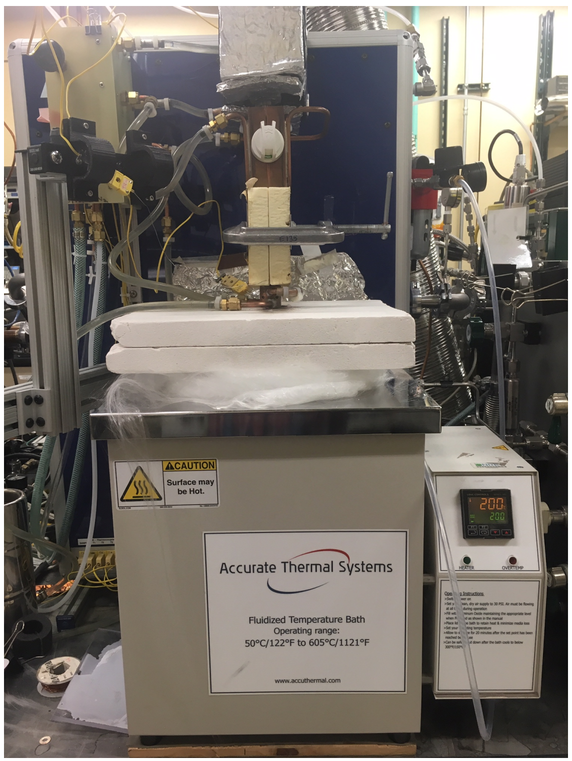


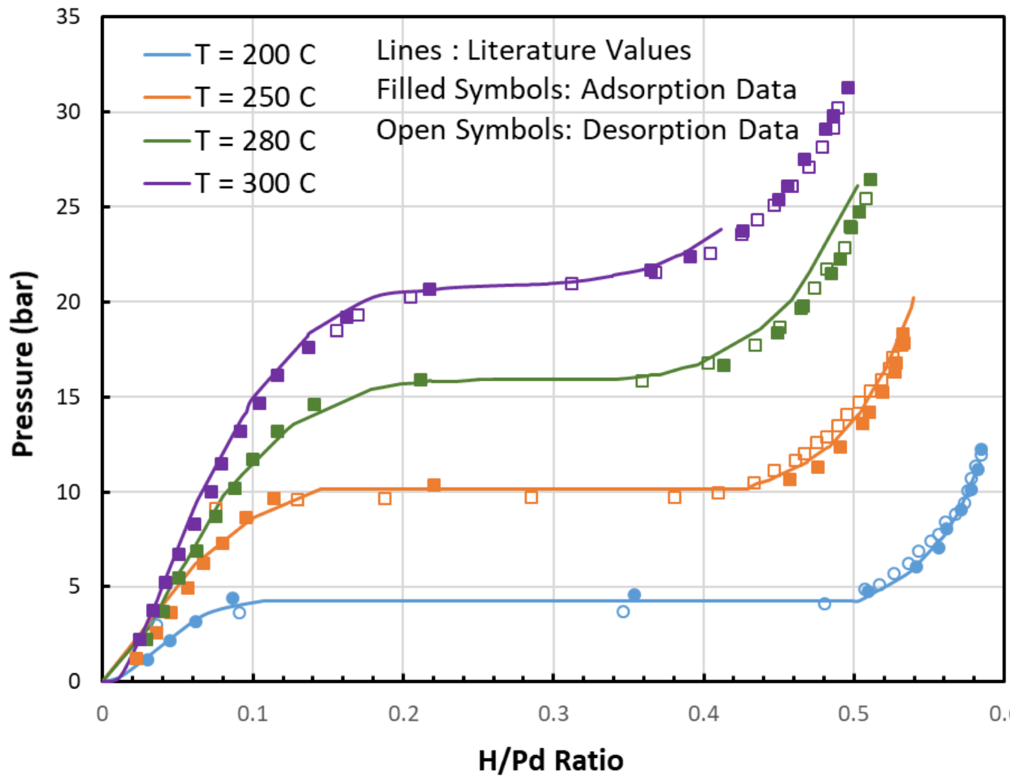


NREL NATIONAL RENEWABLE ENERGY LABORATORY | Sandia National Laboratories | Lawrence Livermore National Laboratory | Berkeley Lab | Pacific Northwest NATIONAL LABORATORY | NIST | SLAC NATIONAL ACCELERATOR LABORATORY

Accomplishment: Task 4a,High temperature validated PCT system

- Provide high temperature PCT validation capability
- Fluidized Bed: T: 30 – 400 ±0.5°C
- Validation using palladium
- Milestone achieved





Accomplishment: Task 4 SLAC capabilities

Technique		Application
X-Ray Diffraction • 25 °C -900°C • Vacuum– 10 bar*	→	**Crystal Structure Solution** • Structure identification of new hydride materials. • Determine dehydrogenation, hydrogenation, and decomposition pathways of hydride materials.
Small Angle Scattering • 25 °C -900°C • Vacuum– 10 bar*	→	**Nanoscale Size Distribution of Particles, Domains, and Pores** • Follow pore opening/collapse during H_2 cycling of hydrides and adsorbents. • Identify porosity infiltration of encapsulated and ALD-coated hydrides.
X-Ray Absorption Spectroscopy • 25 °C -900°C • Vacuum– 10 bar*	→	**Oxidation State and Local Binding Environment** • Determine oxidation states of low Z elements including B, O, and Mg in magnesium borohydride materials. • Determine oxidation states and local binding environment of higher Z elements including Cu and Ni in MOFs and metallated COFs.
X-Ray Raman Scattering • Vacuum– 100 bar*	→	**Oxidation State** • Determine oxidation state of low Z elements in $Mg(BH_4)_2$ materials
X-Ray Photoelectron Spectroscopy • Vacuum– 10 Torr • 25 °C -35°C*	→	**Oxidation State and Chemical Speciation** • Determine oxidation states and chemical speciation of low Z elements in borohydrides and metals in MOFS and metallated COFs.

***Cell development in progress to obtain higher pressures and temperatures**

Accomplishment: Task 5 NREL Seedling Support FY18 – 19

HyMARC Seedling Support FY18 (~ 1 FTE for 6 months)

$NaBH_4$ graphene encapsulation seedling (ANL)

- **Multiple samples were characterized at NREL using TPD-MS (two heating methods), TGA, TEM to determine the extent and effect of graphene encapsulation on $NaBH_4$**

Additives to MgB_2 by mechanical milling seedling (University of Hawaii)

- **Ball milled samples were examined by NREL for H_2 capacity using TPD-MS and TGA**

Fluorinated and metalated COFs seedling (NREL)

- **Two series of metalated COFs were characterized for H_2 sorption properties at NREL via TPD-MS; BET SSA and PSD via nitrogen physisorption**
- **For one COF, heat treatment for Cu-metal reduction was determined by use of TPD-MS and TGA**
- **A series of fluorinated COF pellets were characterized using nitrogen and carbon dioxide physisorption for effect that compression had to BET SSA and PSD**

ALD on $Mg(BH_4)_2$ seedling (NREL)

- **General support of TPD, XRD, SAXs experiments toward milestones**

Electrolyte Assisted Hydrogen Storage Reactions (Liox Power)

- **General support of TPD analysis to determine the composition of the hydrogen desorption stream**

Summary: FY 18 -19 Results Update

- **No-go on modified CN_2 materials**
- **No-go on compaction of PEEK materials**
- **Established a collaboration with Mike Toney at SLAC. Dr. Nick Strange (pd)**
- **Multiple samples for Seedlings were characterized across multiple labs for assessment by DOE for go/no-gos**
- **Variable temperature cryostat controlled PCT apparatus was repaired and re-validated**
- **DOE PEMP Milestone achieved: Milestone: 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**
- **All FY18 Milestones were completed**
- **FY 19-22 HyMARC AOP was completed**
  - **Initiated new materials synthesis, characterization and carriers projects**
  - **Established multiple collaborations across HyMARC teams**
- **www.hymarc.org webpage updated and active**
- **New NDA for HyMARC team and seedlings**
- **Multiple focus area meetings both FTF and video**

Note: FY18 budget was 50% of original plan, all original milestones/deliverables were renegotiated. In August 18 we received funding for initiation of FY19 Phase 2 HyMARC projects.

Future Work & Challenges

Subject to change based on funding levels

- Establish desired ΔG, ΔH, and ΔS for hydrogen storage and carriers
- Determine if metal-catechol modified PEEK materials sites are viable
- Evaluate gated sorbents
- Validate the volumetric capacities for monolith materials
- Optimize the additives in MgB_2 through vapor infusion
- Will ionic liquid borohydrides form eutectic-like systems with metal hydrides
- Evaluate neat porous liquids as carrier sorbents
- Optimize the plasmonic interactions for quick release/adsorption of hydrogen
- Initiate the bio-inspired and FLP-heterolytic systems for hydrogen storage applications
- Support seedlings in Phase 2
- Begin the development of a PCT calorimetry with PNNL
- Validate performance of *in-situ* Raman spectroscopy system
- Validate both hydride and sorbent samples as designated by DOE
- Continue to improve the DataHub

Major Goals

- ***Advance the foundational understanding, develop and characterize the next generation hydrides and/or framework and/or templated materials and/or carbon-sorbents within the hydrogen storage matrix that results in experimental control of:***
    - ***Desorption temperatures***
    - ***Volumetric and gravimetric capacities***
    - ***Kinetic and thermodynamic contributions***
    - ***Materials intrinsic physio-chemical properties***
    - ***Sorption and delivery pressures***
- ***Demonstrate:***
    - ***Volumetric capacities in excess of 50 g/L, to approach the doubling of energy density of 700 bar tanks.***
        - ***Targeted enthalpies in the ideal range of 12-25 kJ/mol***
        - ***Acceptable gravimetric/volumetric capacities and the ability to deliver on-demand H_2 at an appropriate rate and pressure for hydrogen fuel cell vehicles at temperatures approaching 298K and initial overpressure <100bar.***
    - ***Pathway to viable hydrogen carriers and long term storage materials***
        - ***TEA and materials metrics***
        - ***New materials development***
            - ***Define thermodynamic requirements for room temperature adsorption/desorption***
            - ***Porous liquids, eutectics, modified PEEK, FLPs, photocatalysis, compaction improvement.***

Acknowledgements

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Technical back up slides

DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

ST127

Isosteric Heat Calculations

- **3 common ways to calculate isosteric heat**
  - **Explicit T:** $q_{st} = RT^2 \left(\frac{\partial \ln(P)}{\partial T}\right)_n = -R\left(\frac{\partial \ln(P)}{\partial\left(\frac{1}{T}\right)}\right)_n$
  - **Discretized T:** $q_{st} = RT_1T_2\left(\frac{\ln\left(P_2/P_1\right)}{T_2-T_1}\right)_n$
  - ***Ln(P)*** **vs** ***1/T*** **line fit**

- **Objective: Explore implications of equations through models.**
- **How do the model's functional form influence Q_{st} calculations, and more importantly, their interpretation?**

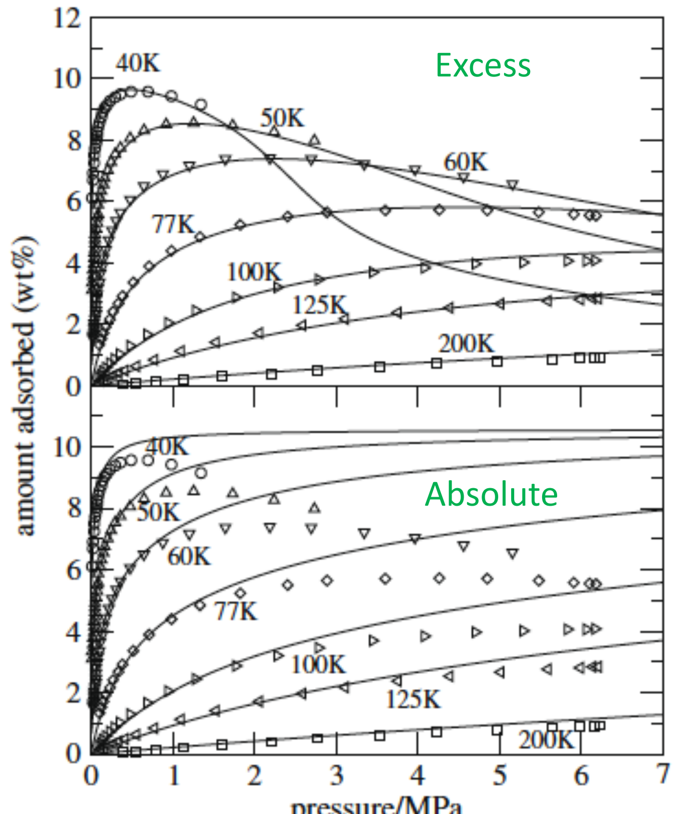
Assumptions:
ideal gas & adsorbed specific volume is negligible.

Double Langmuir With $\sqrt{T}$ Factor From Literature

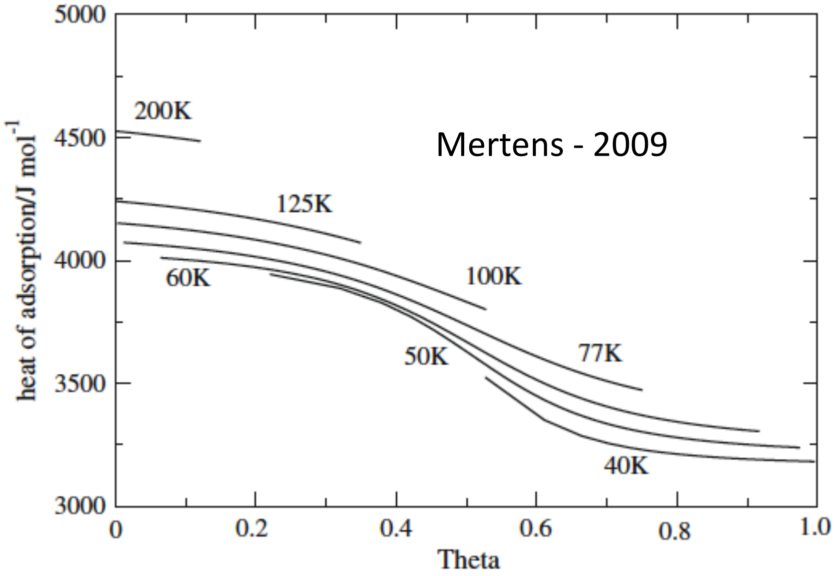
Determination of absolute adsorption in highly ordered porous media

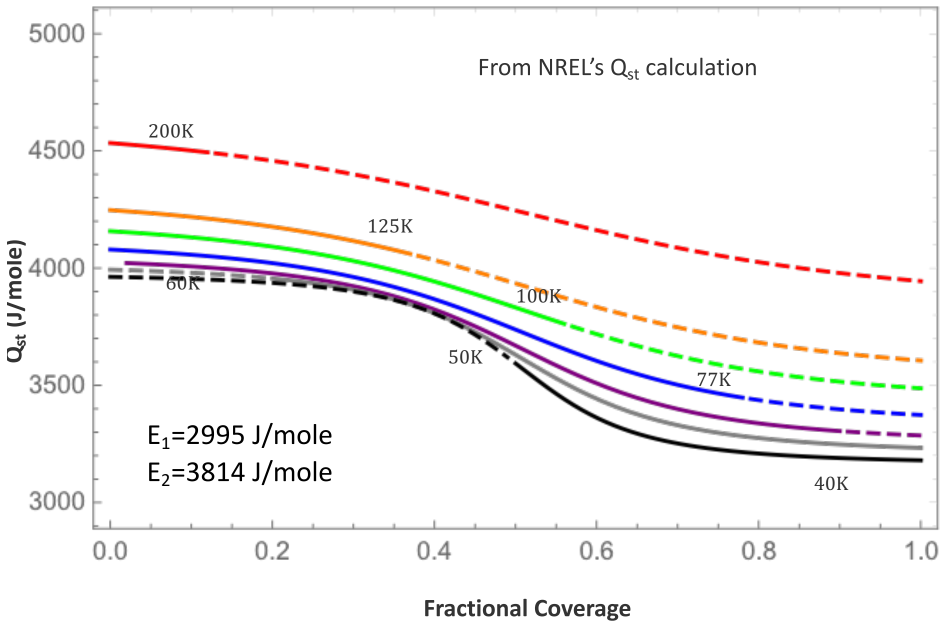
Florian O. Mertens * Surface Science 603 (2009) 1979–1984

- **Used a double Langmuir with $\sqrt{T}$ factor to fit multiple isotherms at all temperatures**
- **Had a term that was used to account for excess to absolute conversion**
- **Used the absolute result to determine Q_{st} at different loadings and temperatures**
- **Choice of isotherm fit dominates the Q_{st} results and does not describe the material**



Mertens Calculated Q_{st}

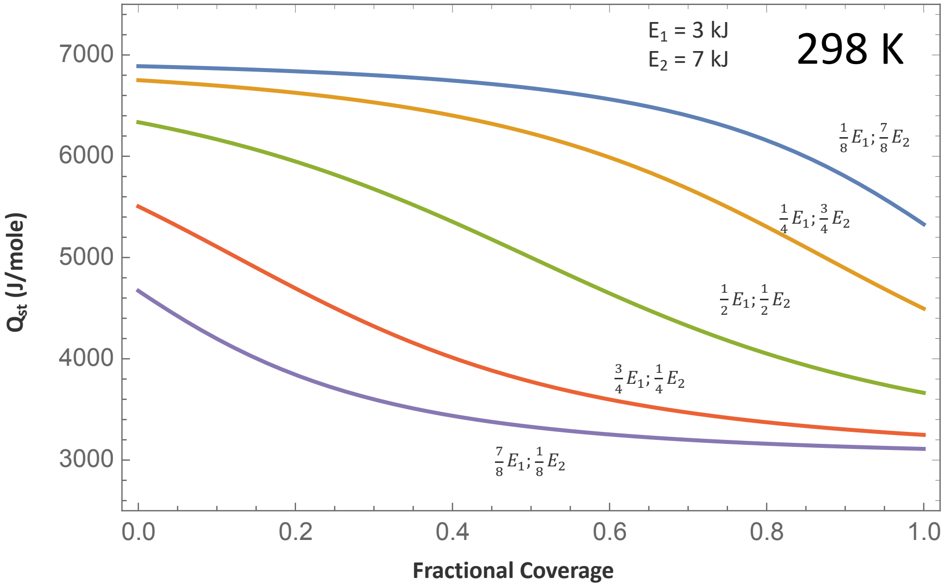


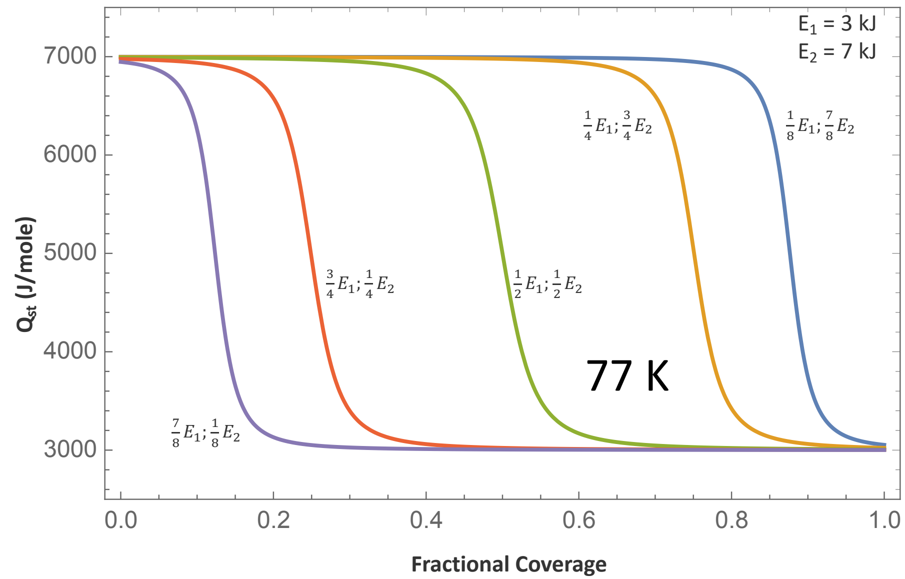


- **Mertens & NREL results are nominally identical.**
- ***Q_{st}* interpretation:**
  - Mertens interprets that Q_{st} changes with temperature & coverage
  - NREL isotherm modeling shows this interpretation is wrong and is an artifact of the initial choice of the isotherm fit
  - Instead there is intrinsic bias with the $\sqrt{T}$ term, and additionally and independently, just reflects how the two sites populate with temperature and coverage (see double Langmuir example)

Isosteric Heat for Double Langmuir Model

Q_{st} Comparison at different site proportions:



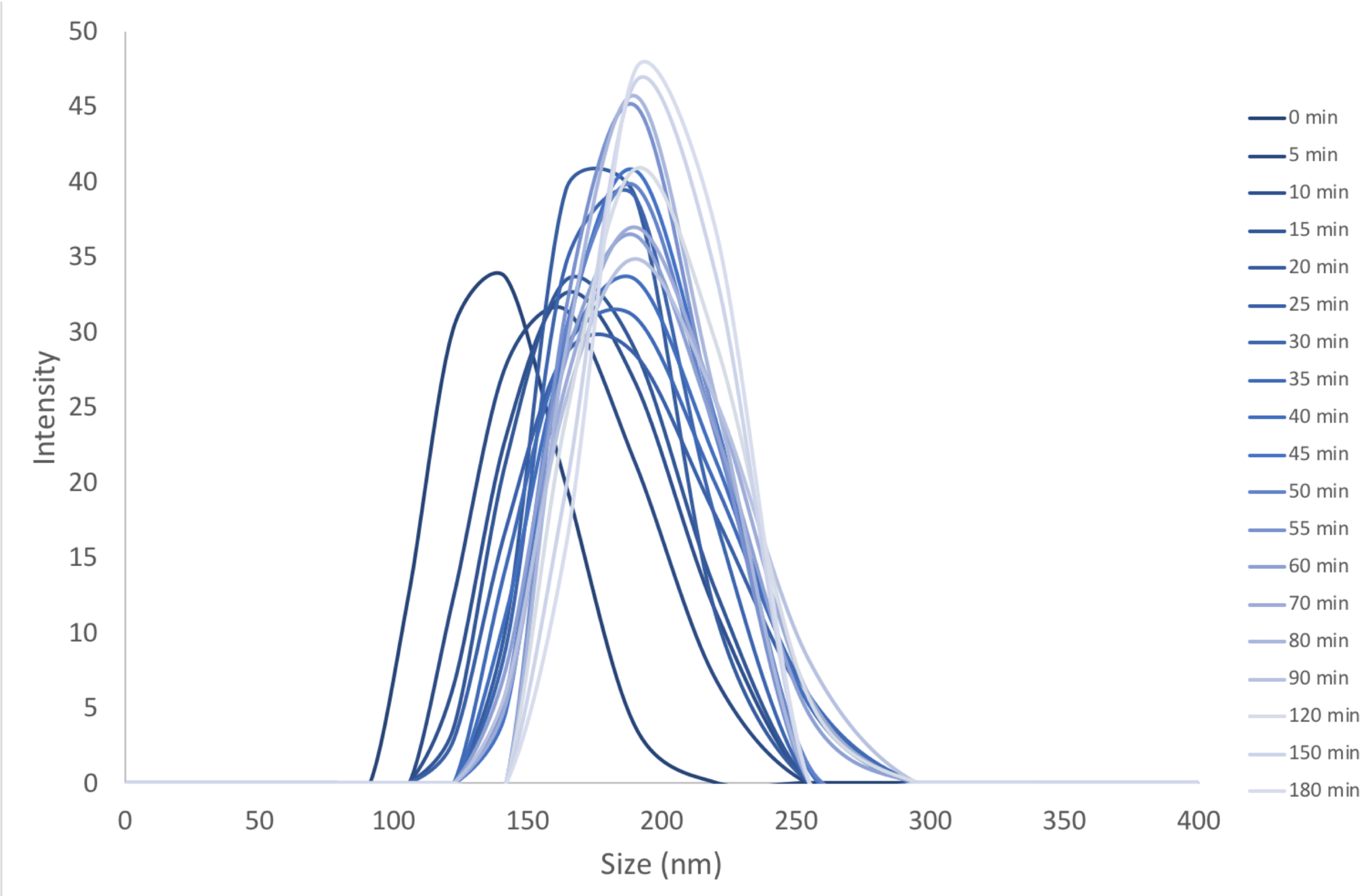


- **General Trends:**
  - As expected, high energy sites tend to get filled first
  - Higher temperatures smear out this trend
  - Q_{st} is just a weighted differential average of how the two sites are filled as a function of coverage and temperature

No $^1/_{\sqrt{T}}$ dependence here

Accomplishment: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

COF 300 growth during synthesis



Reviewer only slides

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Response To FY18 Reviewers' Comments

(A) The proposed future work follows directly from the results obtained in 2017 and 2018. At some point in the characterization/diagnostics effort (relatively near term), it seems that the focus will shift from technique development and formulation of measurement protocols to more routine application of the techniques to provide additional direct support for collaborating partners and seedling projects. Given the concerns about the viability of C2N and Ca oxalate, either as candidate materials in their own right or as model systems for development of more suitable materials, the proposed future work on those materials is questionable. Thoughtful and candid discussions concerning future work, if any, on these systems should be a priority in the newly consolidated HyMARC project.

- We agree with the assessment and at the beginning of FY19 made the decision that we needed to move on from these specific materials. We have incorporated new dynamic COFs and MOFs into the new phase 2 program that are utilizing the knowledge we gained from the model systems.

(B) (1) It would be desirable to gain a deeper understanding of the phenomena and even closer collaboration with simulation groups. (2) Stronger collaboration with groups doing computer simulations, and especially molecular dynamics simulations, could be beneficial.

- We have a new multi-laboratory initiative investigating and advancing several of the fundamental thermodynamic questions that have arisen from our advanced characterization technique results.

(C) The project plan and future scope seem to lack excitement and new ideas.

- We disagree with this statement. In fiscal year 17-18 we were extremely limited in our activities because of the initial 50% cut in funding. In FY19, we have begun to pursue a multitude of new advanced foundational, application, and TEA studies for both transportation and carrier initiatives.

HyMARC Phase 2 Team Milestones

- **Milestone 1: 12/31/18: Focus Area 6.1: Data Hub Determine HyMARC Data Needs:** ***Through meetings between the HyMARC Data Team and technical team members, we will identify data formats, sources and types used across HyMARC. We will develop best practices for data upload and sharing, and usage of defined metadata terms and forms.*** **(100% complete)**

- **Milestone 2: 3/31/19: Focus 3.D.2: Porous liquids as hydrogen carriers:** ***Porous Liquids: Demonstrate viability of click chemistry or nitrene approach for COF shell functionalization.*** **(100% complete)**

- **Milestone 3: 6/30/19: Focus 2.C: Activation of B-B and B-H bonds:** ***Demonstrate computational approach to enable screening of additives to activate B-B bonds in*** MgB_2. **(in progress, on track)**

- **Milestone 4: 9/30/19:** ***Demonstrate >6% reversible capacity for at least one Li-N-H or Mg-N-H phase, based on predicted composition from phase diagram, with reasonable kinetics at a temperature of ≤ 300 ˚C. PCT isotherm measurements will be carried out at temperatures ≤ 300 ˚C measuring total hydrogen uptake and release for each cycle. Isotherm plots and total hydrogen uptake and release data will be provided for each cycle. Data indicating at least 6wt% total hydrogen gravimetric capacity with reasonable kinetics at a temperature of ≤ 300 ˚C will constitute meeting the milestone criteria.*** **(in progress)**

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Publications and Patents

Publications

- M. T. Kapelewski, T. Runčevski, J. D. Tarver, H. Z. H. Jiang, K. E. Hurst, P. A. Parilla, A. Ayala, T. Gennett, S. A. FitzGerald, C. M. Brown, and J. R. Long "Record High Hydrogen Storage Capacity in the Metal–Organic Framework Ni_2(*m*-dobdc) at Near-Ambient Temperatures" *Chemistry of Materials (2018), 30(22), 8179-8189*
- K. E. Hurst, T. Gennett, J. Adams, M. D. Allendorf, R. B.-Xicohténcatl, M. Bielewski, B. Edwards, L. Espinal, B. Fultz, M. Hirscher, M.S.L. Hudson, Z. Hulvey M. Latroche, Di-Jia Liu, M. Kapelewski, E. Napolitano, Z. T Perry, J. Purewal, V. Stavila, M. Veenstra, J. L. White, Y. Yuan, Hong-Cai Zhou, C. Zlotea, and P. Parilla *An International Laboratory Comparison -Study of Volumetric and Gravimetric Hydrogen Adsorption Measurements*" submitted to Chem.Phys.Chem. 2019
- W. Braunecker, K. Hurst, Z. Owczarczyk, M. Martinez, A. Keuhlen, A. Sellinger, J. Johnson. "Phenyl/Perfluorophenyl Stacking Interactions Enhance Structural Order in Two-Dimensional Covalent Organic Frameworks" *Crys. Growth and Des.* 18, 4160, 2018
- M. Dimitrievska, V. Stavila, A. V. Soloninin, R. V. Skoryunov, O. A. Babanova, H. Wu, W. Zhou, W. S. Tang, A. Faraone, J. D. Tarver, B. A. Trump, A. V. Skripov, and T. J. Udovic, The Nature of Decahydro-Closo-Decaborate Anion Reorientations in an Ordered Alkali-Metal Salt: Rb2B10H10, , J. Phys. Chem. C, 2018, 122, 15198-15207.
- M. Dimitrievska, J.-N. Chotard, R. Janot, A. Faraone, W. S. Tang, A. V. Skripov, and T. J. Udovic, Tracking the Progression of Anion Reorientational Behavior between α-phase and β-phase Alkali-Metal Silanides by Quasielastic Neutron Scattering, J. Phys. Chem. C, 2018, 122, 23985-23997.
- M. Dimitrievska, P. Shea, K. E. Kweon, M. Bercx, J. B. Varley, W. S. Tang, A. V. Skripov, V. Stavila, T. J. Udovic, B. C. Wood, Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic LiCB11H12 and NaCB11H12, Adv. Energy Mater., 2018, 1703422.
- M.D. Allendorf, Z. Hulvey, T. Gennett, et.al, An assessment of strategies for the development of solid-state adsorbents for vehicular hydrogen storage, Energy & Environmental Science (2018), 11(10), 2784-2812 (Hot article of 2019)
- C. Sugai, S. Kim, G. Severa, J.L. White, N. Leick, M. Martinez, T. Gennett, V. Stavila, C. Jensen, ChemPhysChem (2019), Ahead of Print.

Patent application:

- Nanostructured composite metal hydrides for hydrogen storage: Christensen, Steven Thomas; Gennett, Thomas; Marius, Noemie; Gross, Karl Joseph U.S. Pat. Appl. Publ. (2018), US 20180333774

Presentations

- -P. A. Parilla, S. Shulda, K. Hurst, T. Gennett, “Determination of Isosteric Heats at Multiple Temperatures”, HyMARC Phase 2 Kickoff Meeting, Phase 1 Summary, Sept., 2018
- -P. A. Parilla, “Liquid-Carrier Hydrogen-Capacity Determination”, HyMARC Phase 2 Kickoff Meeting, Sept., 2018
- -P. A. Parilla, R. Bell, W. Braunecker, S. Christensen, M. Dimitrievska, A. Gaulding, K. Hurst, J. Johnson, N. Leick, M. Martinez, R. Mow, S. Shulda, N. Strange G. Russell-Parks, B. Trewyn, C. Wolden, T. Gennett, “HyMARC Hydrogen Storage Research at NREL”,13th Int. Symposium Hydrogen & Energy, Incheon, Korea, Jan., 2019
- -P. A. Parilla, R. Bell, K. Hurst, N. Leick, M. Martinez, S. Shulda, N. Strange, C. Wolden, T. Gennett, “Thermodynamic Investigations”, Tech. Team Meetings, Feb., 2019
- K.E. Hurst, T.Gennett, and Phil Parila“An International Volumetric Adsorption Measurement Study”,. The American Chemistry Society meeting 2018 New Orleans, LA. 3/20/18.
- A. Gaulding, S. Christensen, J.Urban, N.Leick, T.Gennett Plasmon Interactions for ‘On-Demand’ Hydrogen Release In Hydrogen Carriers Via an Opto-Thermal Process” HyMARC Phase 2 Kickoff Meeting, Sept., 2018
- S. Christensen, N. Leick “HyMARC Seedling: ALD (Atomic Layer Deposition) Synthesis of Novel Nanostructured Metal Borohydrides” FCTO AMR, June 2018
- S. Christensen, N. Leick “HyMARC Seedling: ALD (Atomic Layer Deposition) Synthesis of Novel Nanostructured Metal Borohydrides”, FCTO HSTT, Sept, 12, 2018
- S. Christensen, G. Bentley, T. Gennett Hybrid Inorganic-Organic Bioinspired Materials” Phase 2 Kickoff Meeting, Sept., 2018
- M. Dimitrievska: “Neutron scattering studies of hydrogenous materials for next-generation energy storage”, ACS National Meeting & Exposition, New Orleans, USA, 2018
- M. Dimitrievska: “Role of solvent adducts in hydrogen dynamics of metal borohydrides: neutron-scattering characterization”, ACS National Meeting & Exposition, New Orleans, USA, 2018
- M. Dimitrievska: “Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic LiCB11H12 and NaCB11H12”, MRS Spring meeting, Phoenix, USA, 2018.
- M. Dimitrievska: “HySCORE: Technical Activities at NIST”, DOE-EERE-FCTO Annual Merit Review, Washington DC, USA, 2018
- M. Dimitrievska: “Complex Borohydrides as Superionic Electrolytes”, Review of the NIST Center for Neutron Research at the National Institute of Standards and Technology (NIST), Washington DC, USA, 2018
- M. Dimitrievska: “Neutron backscattering studies of hydrogenous materials for next-generation energy storage”, National Science Foundation Site Visit Review of Center for High Resolution Neutron Scattering (CHRNS), Washington DC, USA, 2018
- M. Dimitrievska: “Role of Solvent Adducts in Hydrogen Dynamics of Metal Borohydrides—Neutron-Scattering Characterization”, American Conference on Neutron Scattering, Collage Park, MD, USA, June 2018

Presentations

- Jensen, Craig M.; Nguyen, Phuong Q.; Chong, Marina; Shrestha, Sunil; Autrey, Tom; Bowden, Mark; Gennett, Thomas; Yang, Junzhi High capacity hydrogen cycling between magnesium borohydride and magnesium boranes under moderate conditions ACS National Meeting, New Orleans, LA,2018
- Gennett, Thomas; Parilla, Philip Hydrogen storage characterization and optimization research effort, HySCORE ACS National Meeting, New Orleans, LA, 2018
- Shulda, Sarah; Blackburn, Jeffrey; Parilla, Philip; Gennett, Thomas Identifying hydrogen adsorption sites using in-situ DRIFTS ACS National Meeting, New Orleans, LA, 2018
- Hurst, Katherine; Gennett, Thomas; Parilla, Philip, Results from a multi-laboratory comparison of hydrogen volumetric capacity measurements ACS National Meeting, New Orleans, LA, 2018
- Nguyen, Phuong Q.; Chong, Marina; Bowden, Mark; Shrestha, Sunil; Yang, Junzhi; Gennett, Thomas; Autrey, Tom, Jensen, Craig M. Role of solvent on selective dehydrogenation of magnesium borohydride at moderate conditions ACS National Meeting, New Orleans, LA 2018
- Bell, Robert T.; Leick, Noemi; Olsen, Michele; Gennett, Thomas; Parilla, Philip, System allowing automated thermal conductivity mapping as a function of temperature and pressure for hydrogen storage materials ACS National Meeting, New Orleans, LA, 2018
- Gennett, T. et. Al., HySCORE: NREL Technical Activities, DOE-FCTO AMR Washington, DC, June 2018.
- Gennett, T. Allendorf, M.D. HyMARC: A Consortium for Advancing Hydrogen Storage Materials, DOE-FCTO AMR Washington, DC, June 2018.
- Gennett, T. et. al., NREL HyMARC Research Overview, US Car Tech Team review, Detroit, MI 2019
- Gennett, T. Allendorf, M.D., HyMARC: Addressing Key Challenges to Hydrogen Storage in Advanced Materials Through a Multi-Lab Collaboration US Car Tech Team review, Detroit, MI 2019
- R.E. Mow, M.B. Martinez, T. Gennett, W.A. Braunecker Porous liquid covalent organic frameworks. ACS National Meeting, Orlando, FL, 2019
- N. Leick, V. Stavila, K. Gross, M. Bowden, T. Gennett, S.T. Christensen Role of additives on the H2 storage properties of Mg(BH4)2. ACS National Meeting, Orlando, FL, 2019
- R.T. Bell, G. Russell-Parks, A. Huffer, S. Shulda, M.B. Martinez, P. Parilla, T. Gennett, B.G. Trewyn Ionic liquid additives for lowering the melting point of magnesium borohydride. ACS National Meeting, Orlando, FL, 2019
- R.T. Bell, G. Russell-Parks, A. Huffer, S. Shulda, M.B. Martinez, P. Parilla, B.G. Trewyn, T. Gennett Tracking the Mg(BH4)2/diglyme liquidus curve from room temperature to Mg(BH4)2-rich eutectic. ACS National Meeting, Orlando, FL, 2019
- W.A. Braunecker, M.B. Martinez, K.E. Hurst, S. Shulda, J.T. Koubek, A. Sellinger, T. Gennett, J.C. Johnson Hydrogen sorption in fluorinated organic frameworks. ACS National Meeting, Orlando, FL, 2019

Task 1: Issues with Isosteric Heat Determination

Experimental:

- Adequate isotherm data collection
- Sensitivity analysis to calibration errors

Analysis:

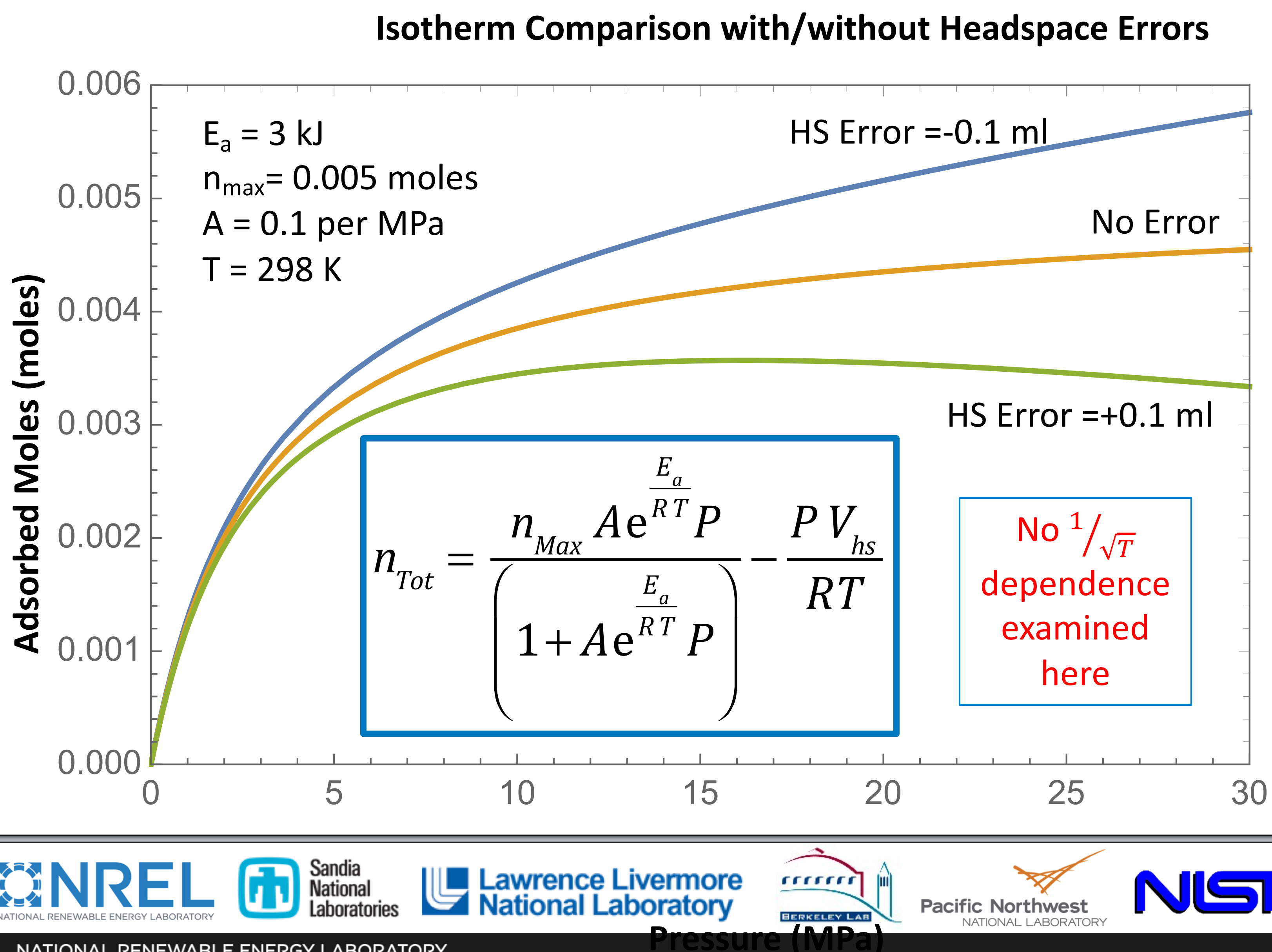
- Fitting/Interpolation
- Best isotherm data fitting
- Excess vs absolute capacity
- Appropriate Q_{st} equation model

$$\frac{\partial P}{\partial T} = \frac{\bar{s}_1 - \bar{s}_2}{\bar{v}_1 - \bar{v}_2} = \frac{Q_{st}}{T(\bar{v}_1 - \bar{v}_2)}$$

- **Analysis (cont):**
  - High pressure effects (supercritical region)
  - Q_{st} calculation protocol
  - Temperature effects & Temperature-dependence assumptions
  - Heterogenous adsorption sites
  - Determining equilibrium constant, K(T)
  - Validity of van't Hoff

$$\ln K(T) = -\frac{\Delta H^o}{R\,T} + \frac{\Delta S^o}{R}$$

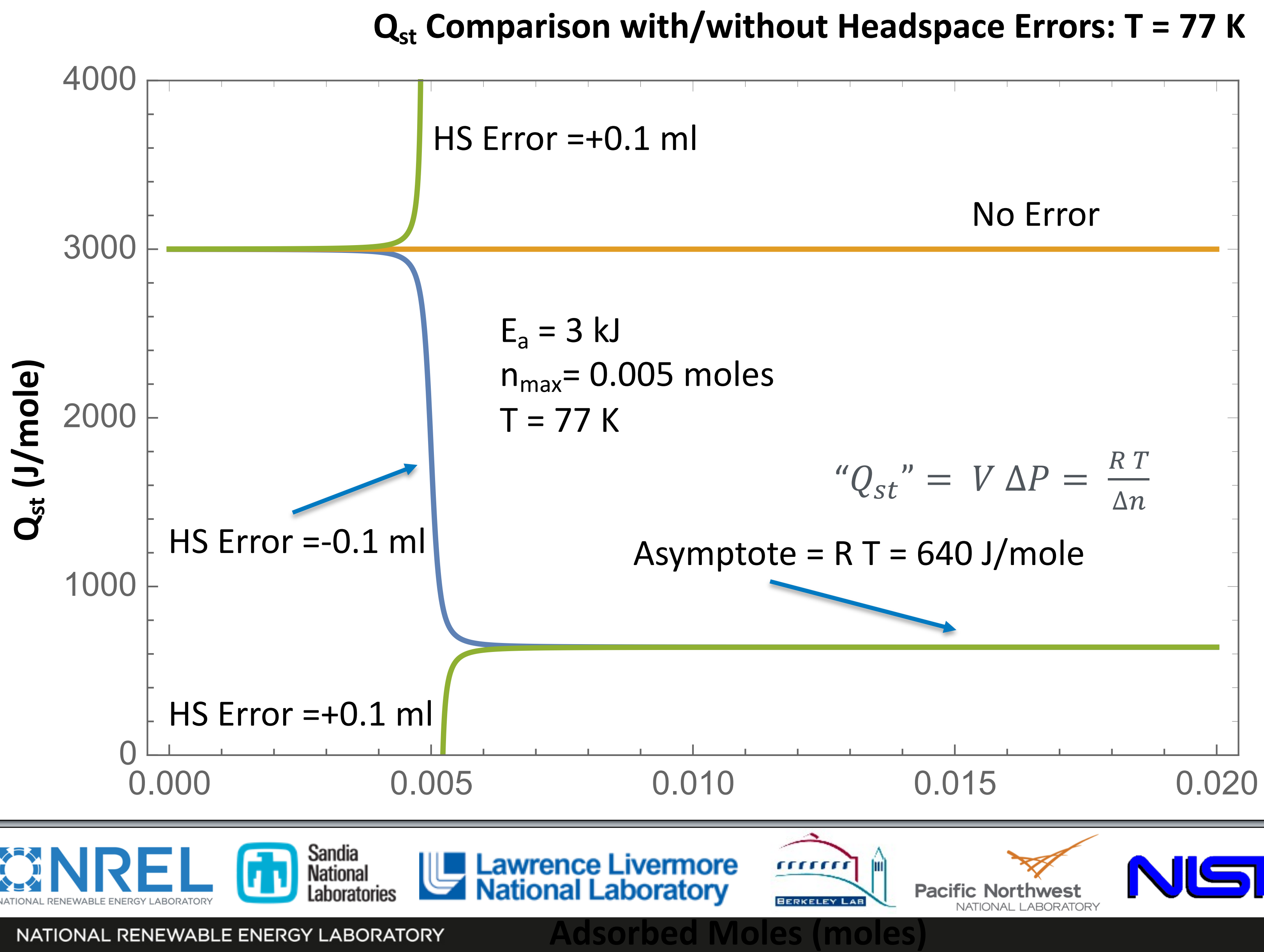
Task 1: Isosteric Heat for Langmuir Model with Calibration Error



$$n_{Tot} = \frac{n_{Max} A e^{\frac{E_a}{RT}} P}{\left(1 + A e^{\frac{E_a}{RT}} P\right)} - \frac{P V_{hs}}{RT}$$

No $^1/_{\sqrt{T}}$ dependence examined here

Task 1: Isosteric Heat for Langmuir Model with Headspace Error



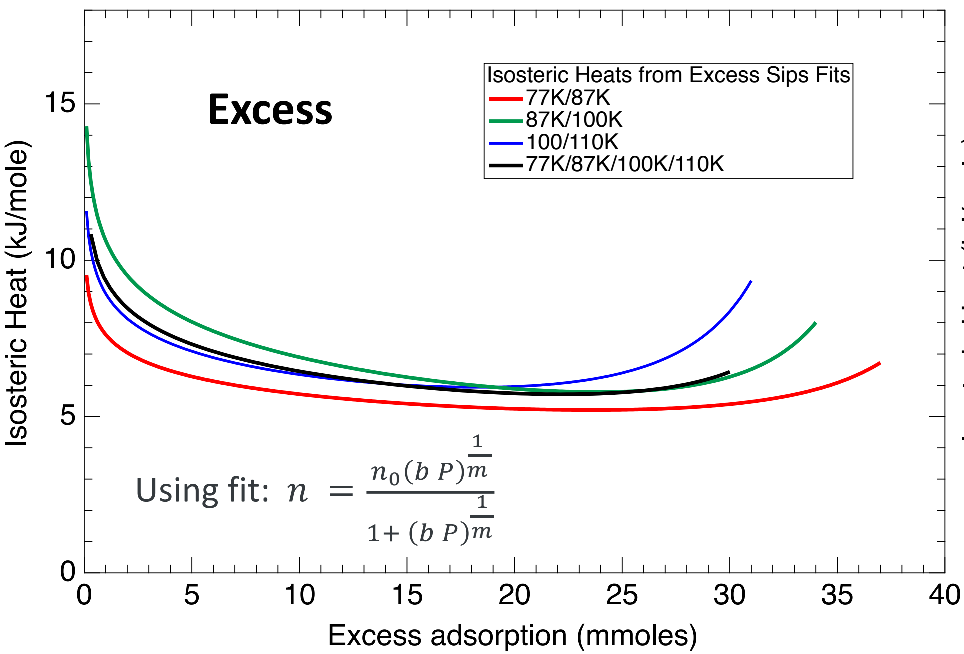
Task 1: Conclusions for Headspace Error

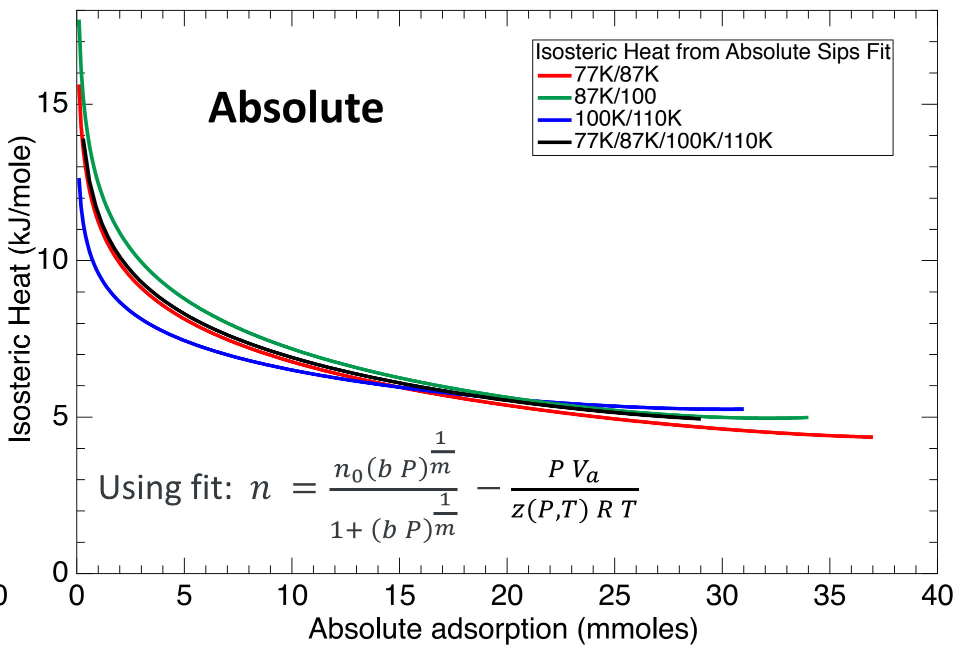
All measured isotherms have "headspace" error

- All measured isotherms are determining excess capacity, but absolute capacity is needed for Q_{st} calculation; this can be viewed as a "headspace" error for absolute capacity (Parilla, et al, Appl. Phys. A, 2016).
- Additional errors in determining actual (excess) headspace calibration must then be added to this.
- Asymptote is the "Q_{st}" of free gas ($V\ \Delta P\ work = R\ T/\Delta n$)

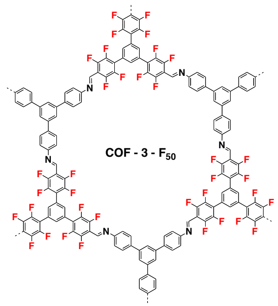
Task 1: Isosteric Heat: Using Excess vs Absolute

- **Comparison of Q_{st} from Excess & Estimate of Absolute**
- **From Cryo-PCT Milestone Data**
- **Conversion of excess to absolute was accomplished by including a $\frac{P\,V_a}{z(P,T)\,R\,T}$ term in the Sips isotherm fit**
- **Absolute shows more overall consistency, but has more variation at low coverage**
- **This is probably due to the steepness of the isotherm at low coverage and how well the fit matches the data**

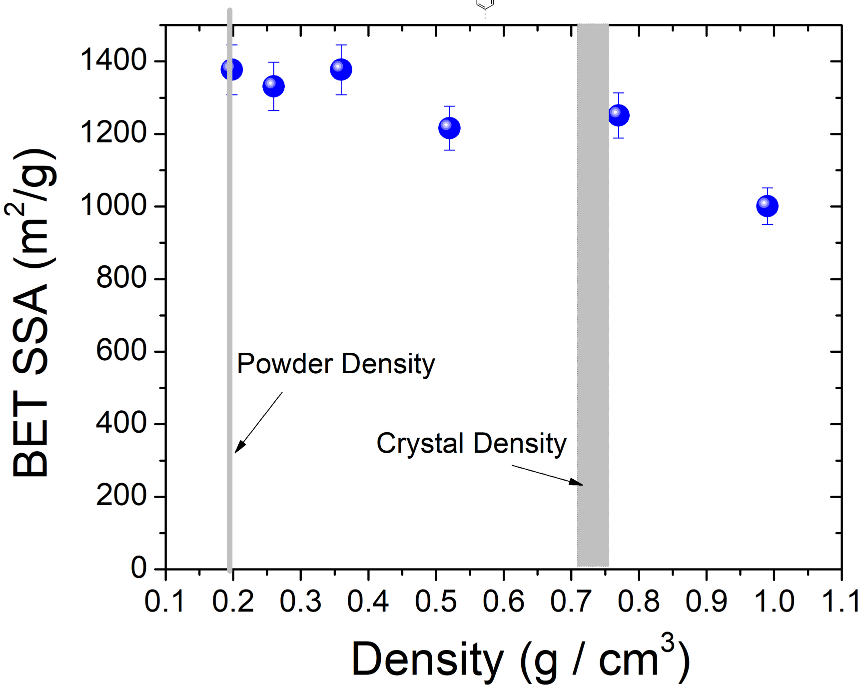




Task 1: COF Densification Studies for seedling

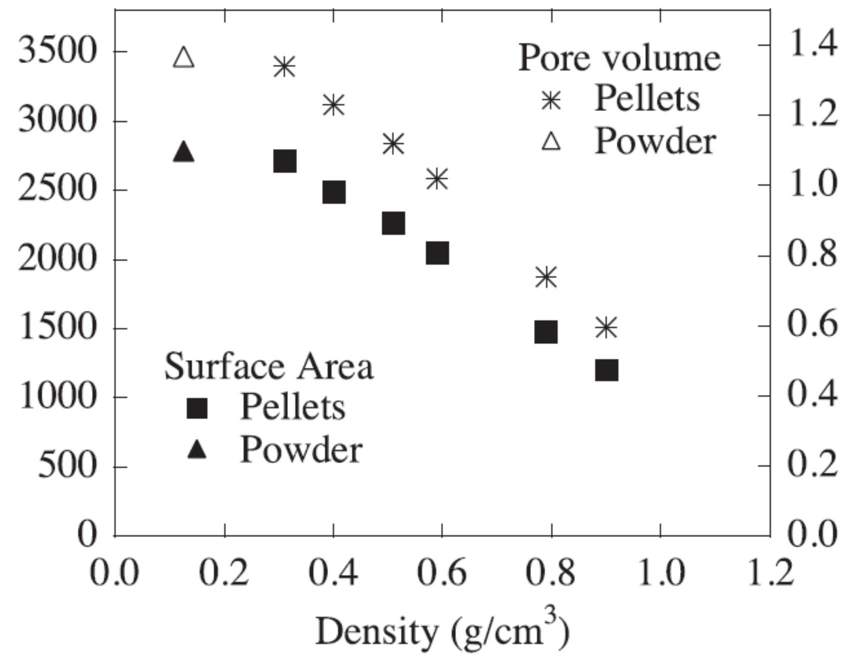


COF-3



MOF-5

Int. J. Hydrogen Energy **2012**, *37* 2723-2727



XRD and PSD suggest up to crystal density, order is maintained and large pore void space is eliminated

Task 2: B-B Bond Current Materials synthesized

Temperature Programmed Desorption, X-Ray diffraction, Nuclear Magnetic Resonance, PCT and DRIFTS characterization planned for most promising materials

MgB_2-based materials:

<u>THF-study:</u>

MgB_2 + 5pulses THF@250˚C
MgB_2 + 5pulses THF@350˚C
MgB_2 + 10pulses THF@350˚C
MgB_2 + 15pulses THF@350˚C
MgB_2 + 25pulses THF@350˚C

$Mg(BH_4)_2$-based materials:

<u>THF-study:</u>

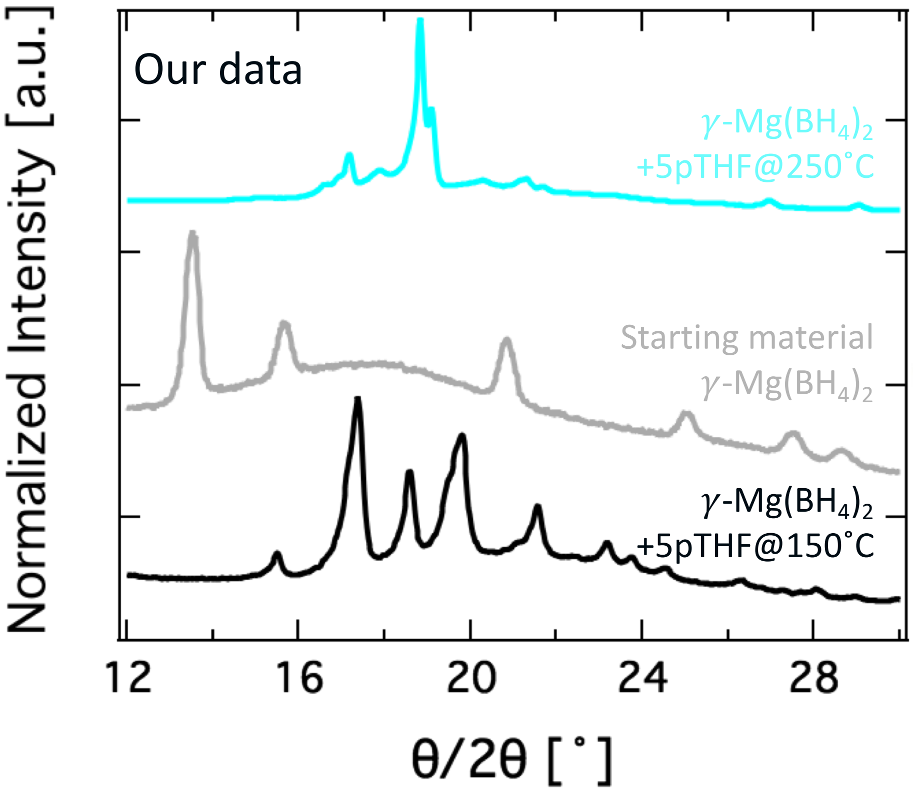
γ-$Mg(BH_4)_2$ + 1pulse THF@50˚C
γ- $Mg(BH_4)_2$ + 5pulses THF@50˚C
γ- $Mg(BH_4)_2$ + 25pulses THF@50˚C

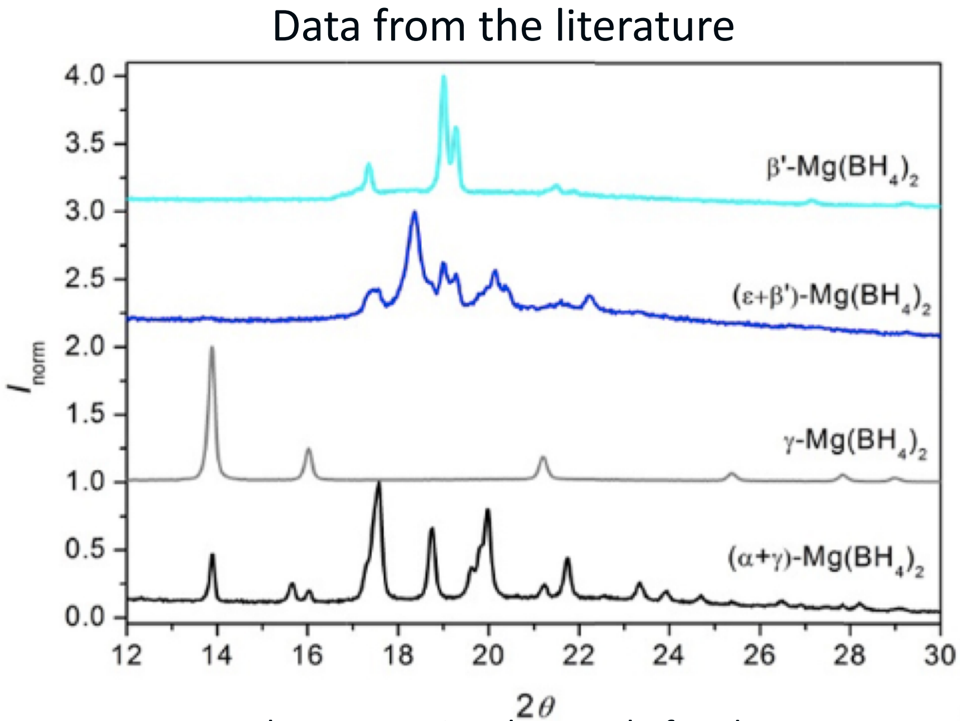
γ- $Mg(BH_4)_2$ + 5pulses THF@150˚C

γ- $Mg(BH_4)_2$ + 1pulses THF@250˚C
γ- $Mg(BH_4)_2$ + 5pulses THF@250˚C
γ- $Mg(BH_4)_2$ + 25pulses THF@250˚C

γ- $Mg(BH_4)_2$ + 5pulses THF@350˚C

Task 2: Accomplishment: $Mg(BH_4)_2$+THF Crystal Structure





O. Zavorotynska, International Journal of Hydrogen Energy **41** (32), pp. 14387-14403 (2016)

<u>Initial results suggest:</u>

- While there are subtle peaks, the phase of the borohydride is changing as a function of temperature:
  - γ-$Mg(BH_4)_2$ +5pTHF@250˚C changed into β- $Mg(BH_4)_2$
  - γ-$Mg(BH_4)_2$ +5pTHF@150˚C changed into (α+γ)- $Mg(BH_4)_2$

Task 2: Status of the BN sorbent work

Relevance: BN has a theoretical capacity of ~6wt% but has thus far not been achieved. A new theory claims that defects in the hexagonal BN lattice structure could be responsible for the high capacity.

Approach: Introduction of defects in the hexagonal BN lattice through plasma treatments and potentially ion implantation techniques.

Current status:

BN synthesized at LBNL from melamine and boric acid by J. Urban's group
500 mg shipped to NREL and 3 different plasma treatments were done:
Ar plasma
Ar/N_2 plasma
Ar/O_2 plasma
Temperature programmed desorption is ongoing

Future plans:

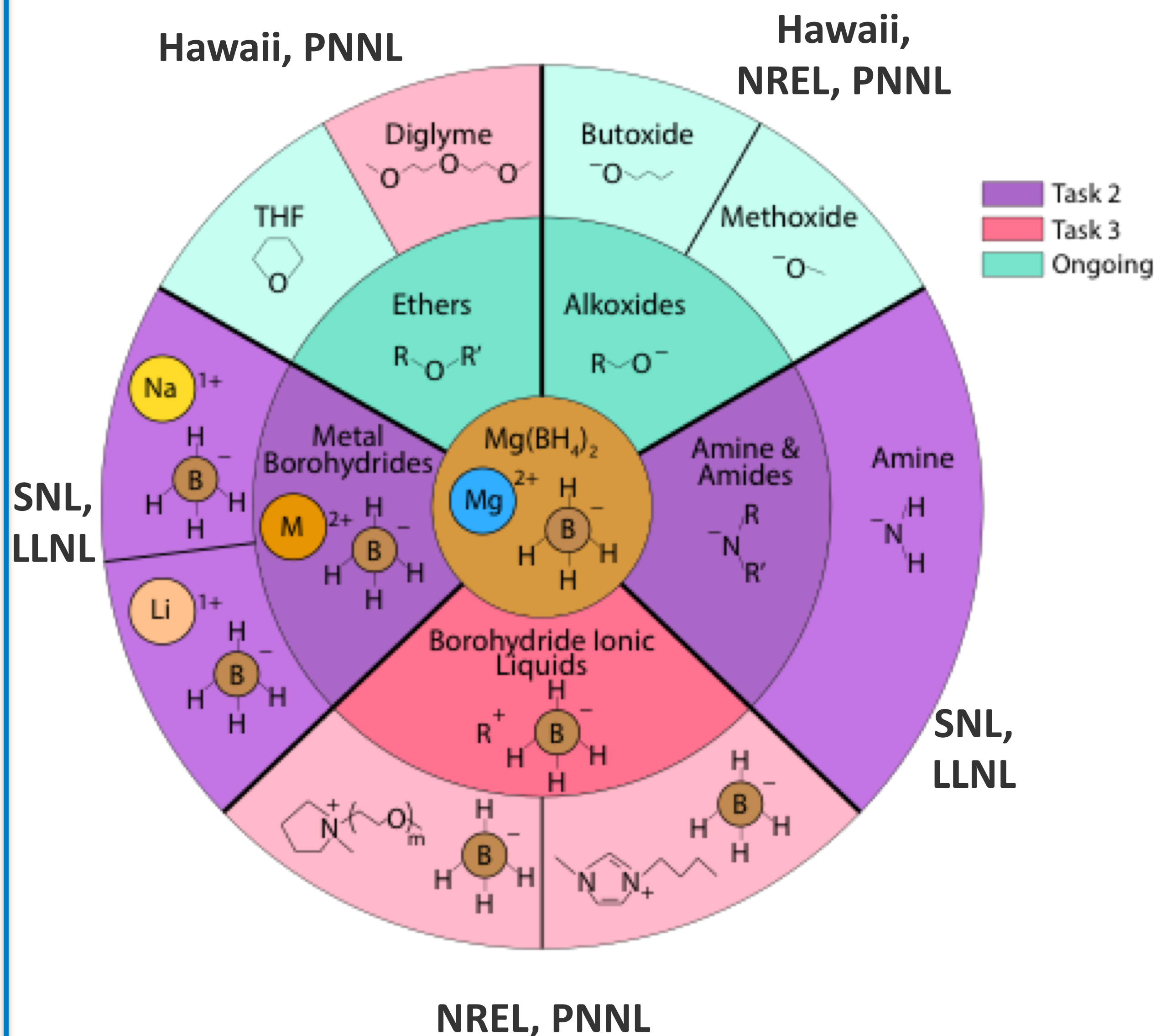
If the BN is stable in ambient conditions, ion implantation will be performed
The material showing the best improvement in capacity will be scaled up for PCT measurements and ex situ diagnostics (XRD, NMR, XPS)

Task 3.C Liquid hydride systems as hydrogen carriers (eutectics, ionic liquids, etc)

Concept: *Increase hydride kinetics, decrease operating temperatures, and control reaction pathways through additives.*

Science question: *Evaluate whether additives can lower hydride melting points, allow cyclability, and prevent irreversible reaction dead-ends.*

Approach: *Analyze the phase-spaces and stability of hydride / additive systems, beginning with organic-cation borohydrides with tunable melting points and properties.*



Task 6: HyMARC EMN Data Hub

"The EMN Data Hubs support collaborative science through the establishment of an accessible, searchable data resource"

The Data Hub is a "Virtual Lab" for the EMN Consortium

- Secure sharing of data among project team members.
- Advanced search across all data (you have permissions to) using defined metadata.
- Facilitate access to advanced data tools for analysis.
- Make selected datasets publically available.
- Fulfills DOE's requirement for establishing an EMN data resource.

https://datahub.HyMARC.org

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · Lawrence Livermore National Laboratory · Berkeley Lab · Pacific Northwest National Laboratory · NIST · SLAC National Accelerator Laboratory