NREL
NATIONAL RENEWABLE ENERGY LABORATORY

HyMARC
Hydrogen Materials Advanced Research Consortium

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**

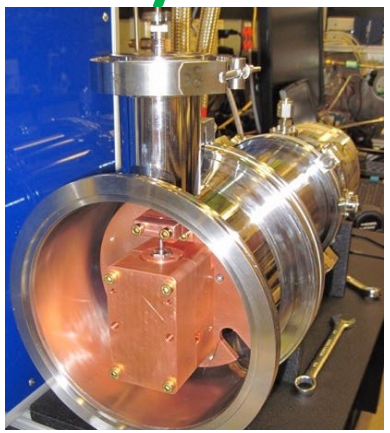
NREL Approach: Focus Areas: Black–active (AMR slides), Purple-active, Blue-future

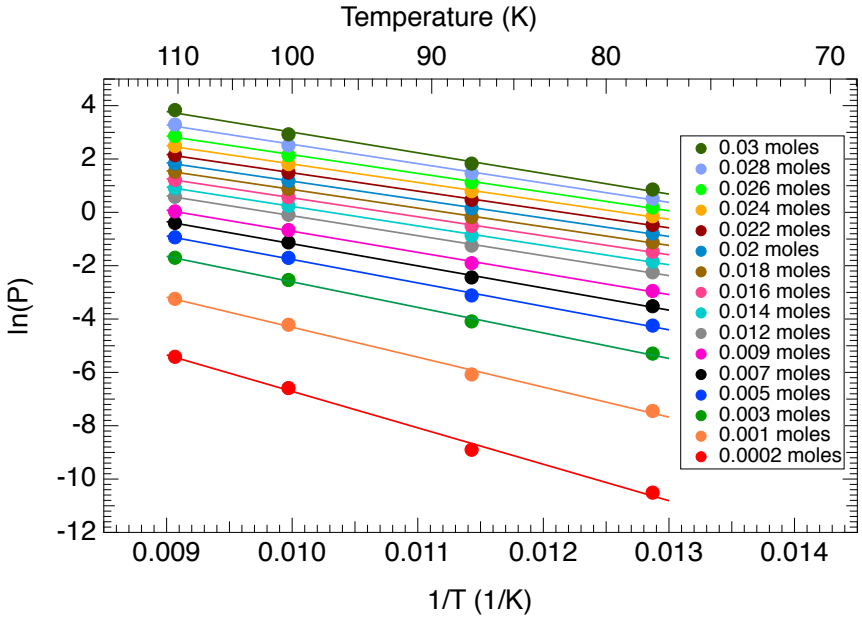
- **Task 1 Sorbents**
  - 1.A Focus Area: Enthalpy / Entropy and Isosteric Heat. (Q_{st})
  - 1.B Focus Area: Optimizing Sorbent Binding Energies (starts Q3-FY19)
  - 1.C Focus Area: Optimizing of Sorbent Packing (rev. only slide)
  - 1.D Dynamic Sorbent Materials (Starts Q4 FY19)
- **Task 2 Hydrides**
  - 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)**

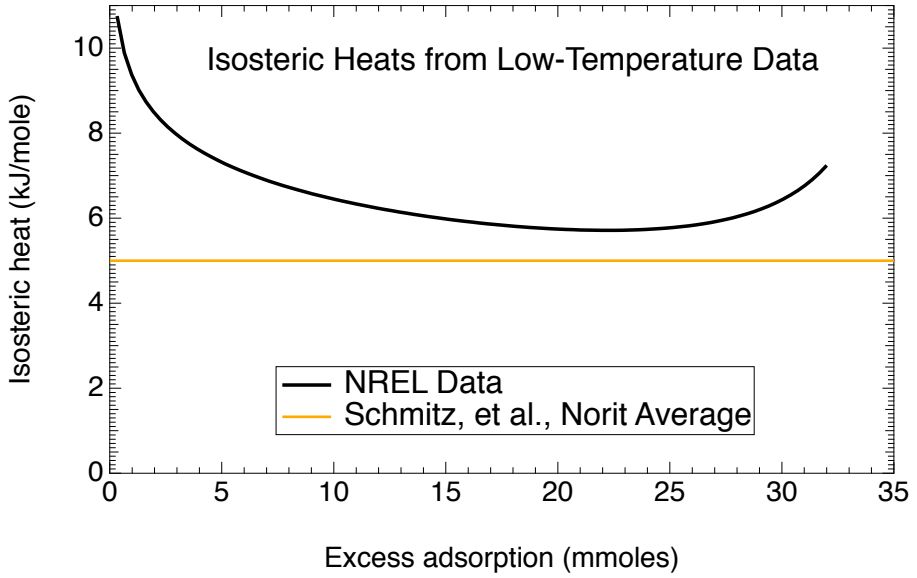
Accomplishment: Task 1a Enthalpy/Entropy and Isosteric Heat. (Q_{st})

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

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

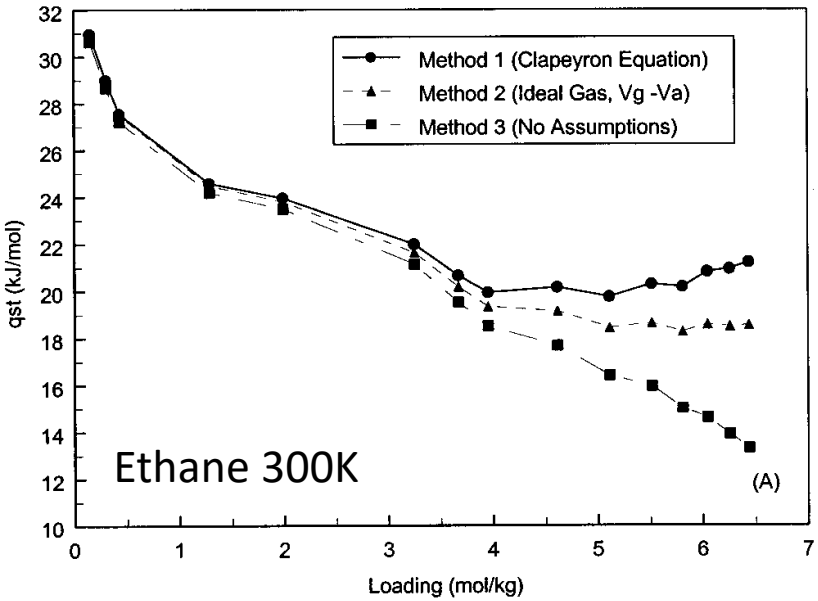
Langmuir **1998**, *14*, 6323−6327

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

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

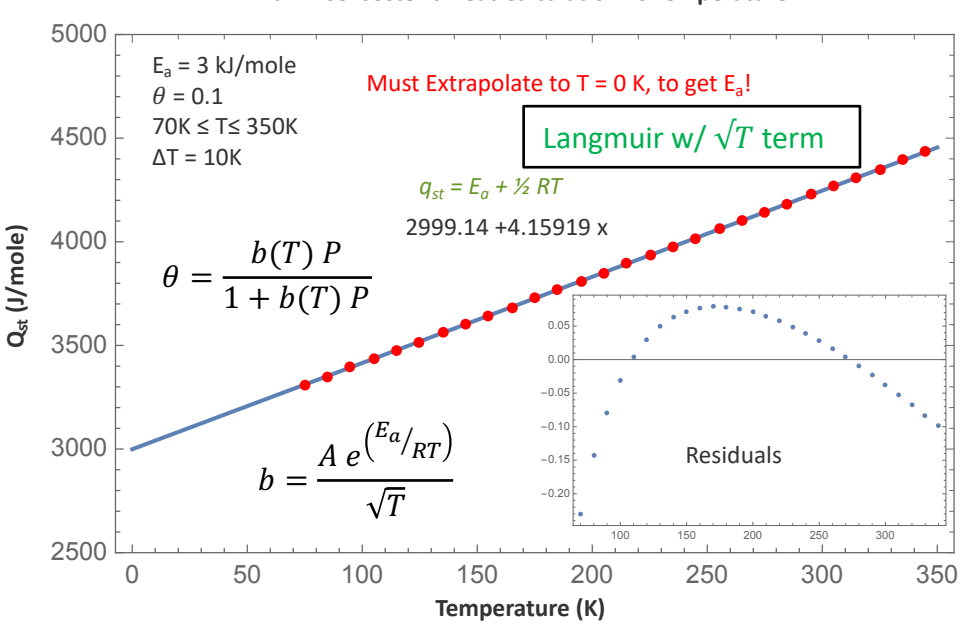


Accomplishment: Task 1a Enthalpy/Entropy and Isosteric Heat. (Q_{st})

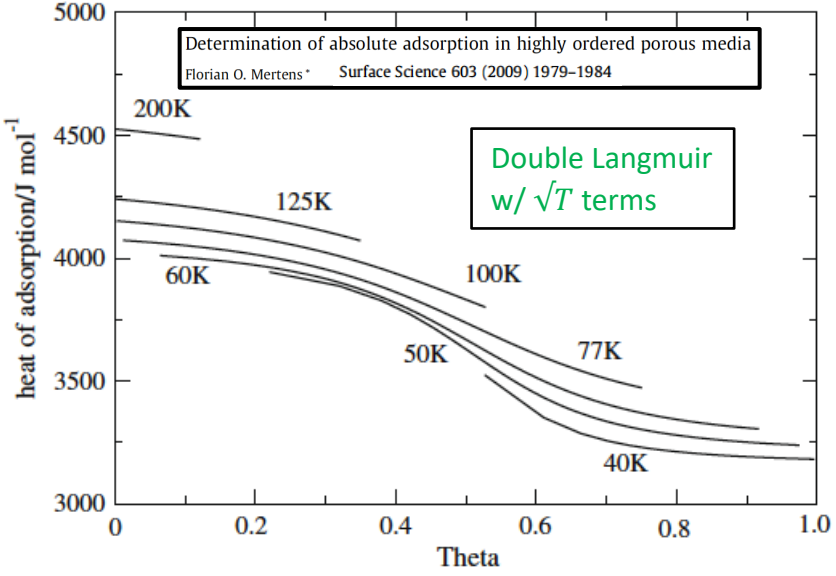
Issues Investigated with Isosteric Heat Determination

- 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

NREL Modeling



Example from the literature



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

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]

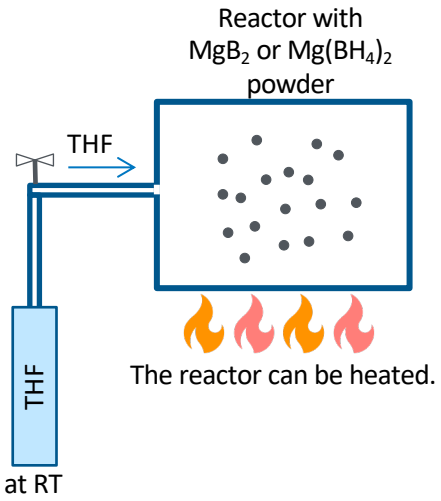
Uniqueness of this project:

- 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.

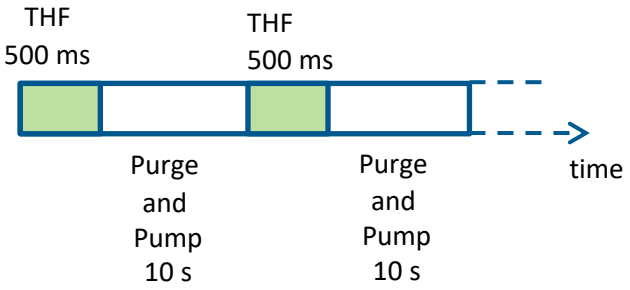
[1] Severa *et al.*, ChemPhysChem 2019, 20, 1–5 (HyMARC)
[2] Severa *et al.*, *Chem. Commun.*, **46**, 421–423 (2010)
[3] PNNL: Chong *et al.*, *Inorganics*, **5**, 89 (2017)

Experimental:

Setup



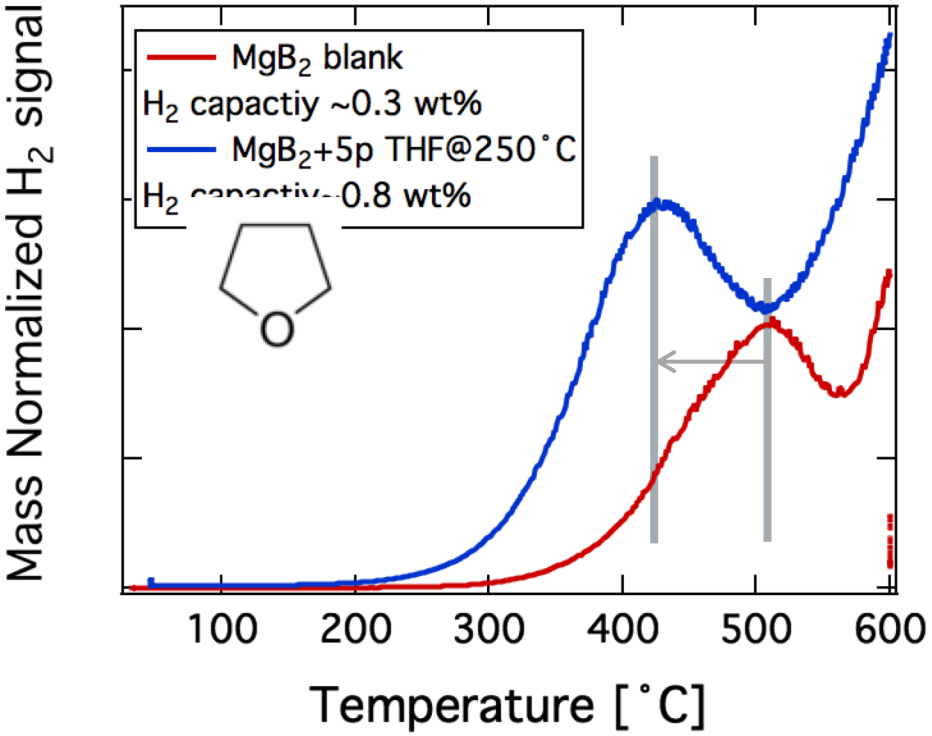
Pulse Sequence



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

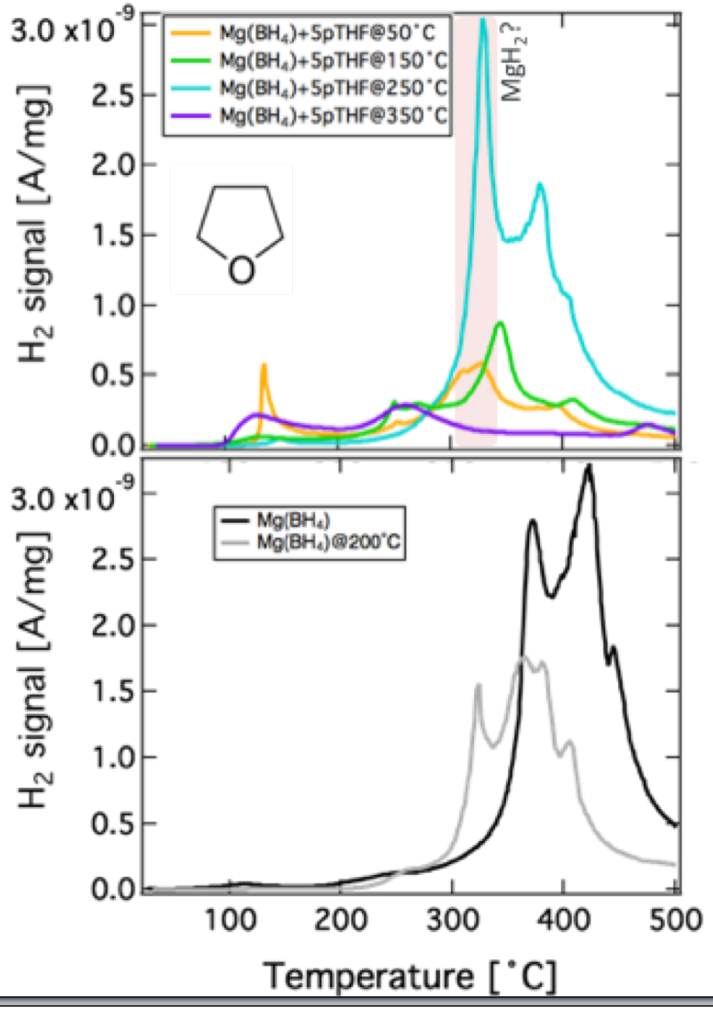
Sample	MgB2 + 25 p THF @ 350 °C	MgB2- Neat
Mass (mg)	134	329
Degas Temp (˚C)	250	250
Dosing Temp (˚C)	250	250
Time (hrs)	50	48
Nominal Pressure (bar)	120	127
Total ΔP (bar)	0.570	0.678
H_2 adsorbed (mmol)	0.170	0.202
H_2 adsorbed (mg)	0.339	0.403
Wt %	0.25±0.05%	0.12±0.02%

Initial results suggest:

- 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

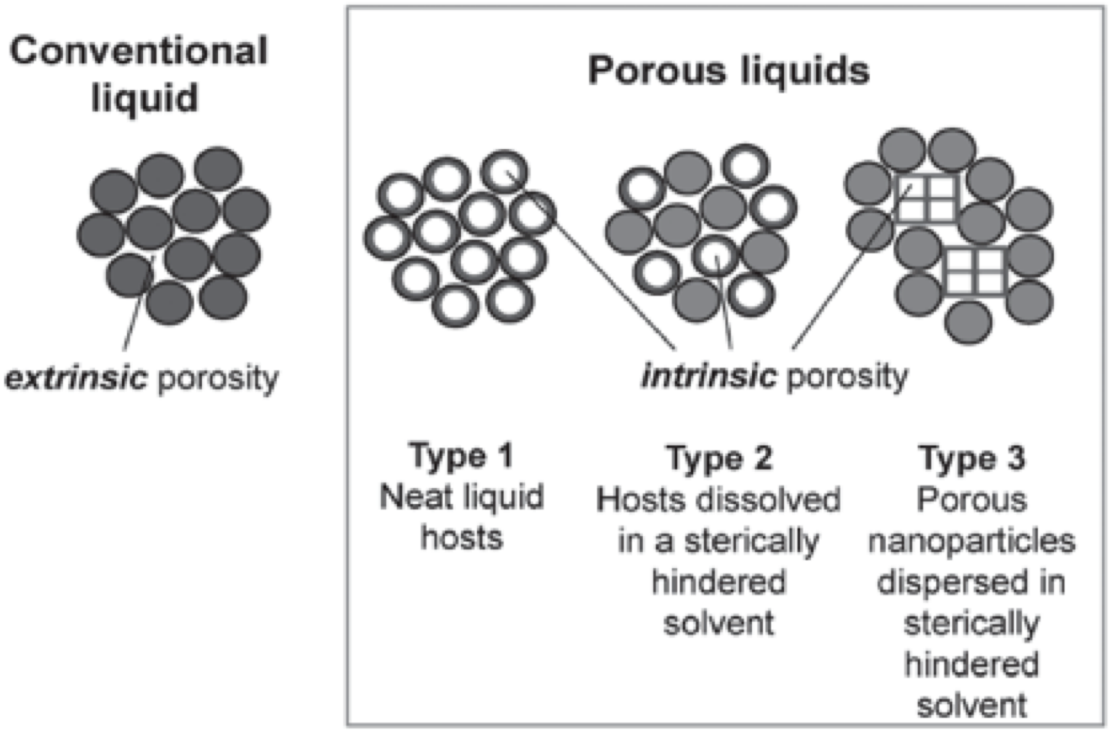


Initial results suggest:

- 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)

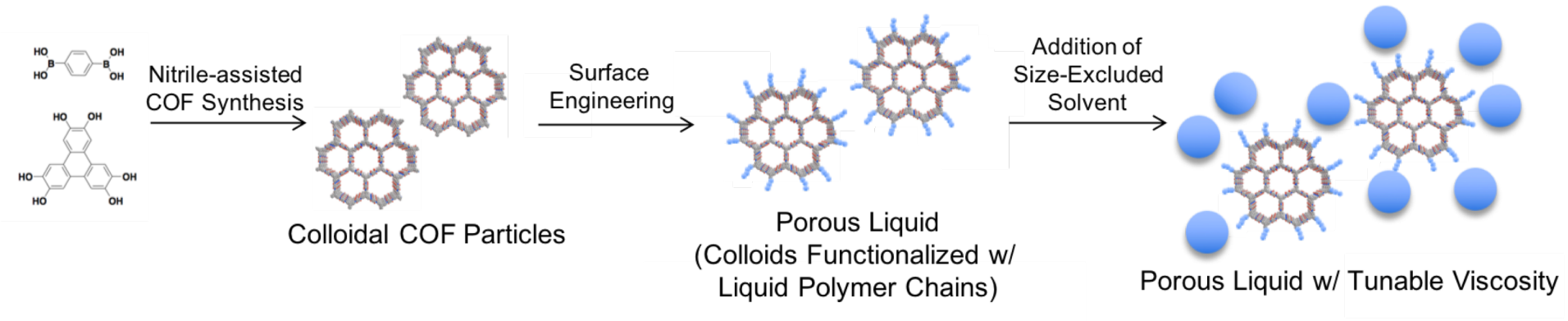
Conventional liquids only have extrinsic porosity, i.e., small transient and ill-defined pores, while the three types of porous liquids have intrinsic permanent porosity.



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 $H_{2(g)}$)**

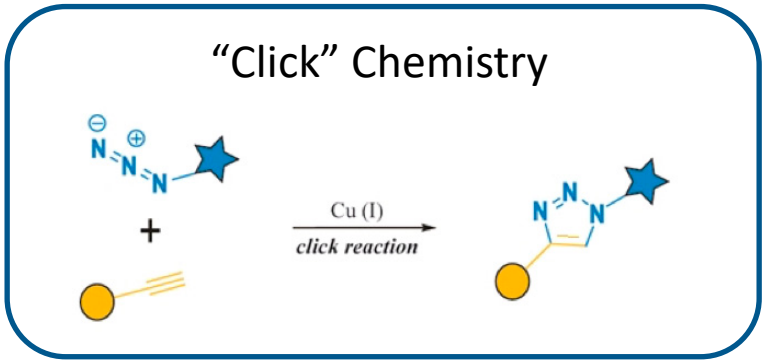
Approach: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

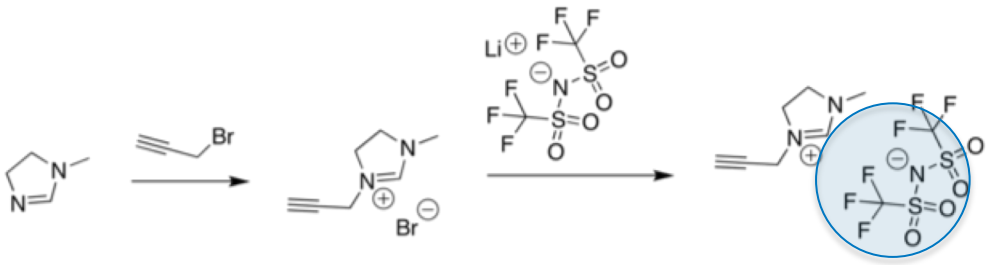


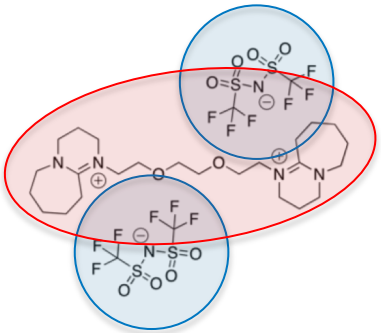
- COFs could provide unparalleled fine-tuning of gas selectivity/separation in porous liquids
- Consideration to (1) COF particle size, (2) COF pore size & co-solvent, (3) Functionalization
- Functionalization strategies: click chemistry of liquid polymer chains and/or tethered ILs

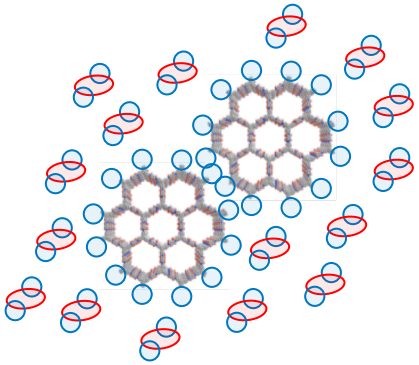
Approach: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

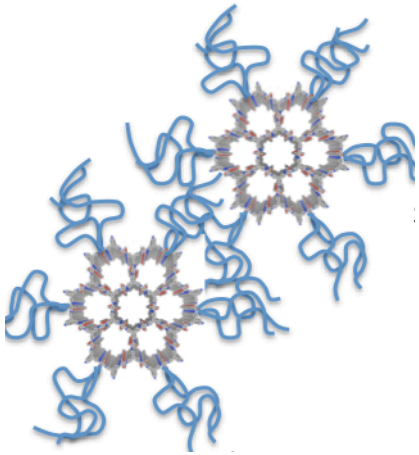
Click Chemistry Functionalization of COF





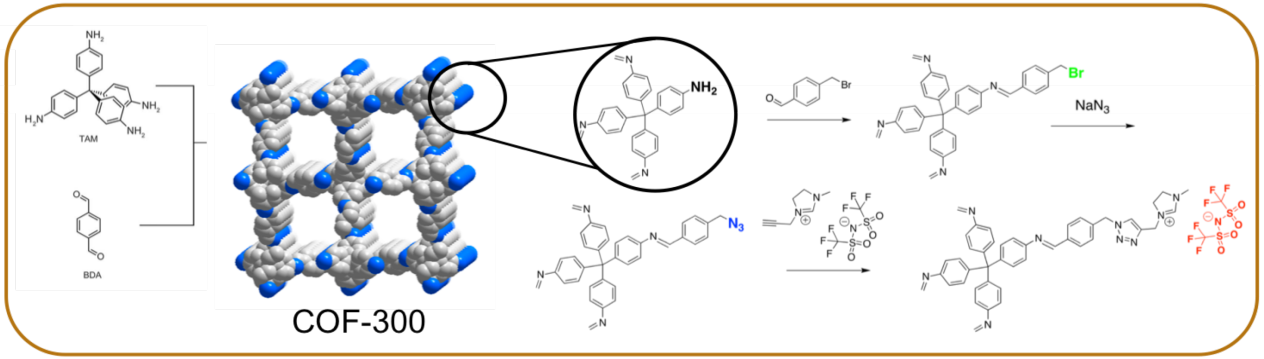


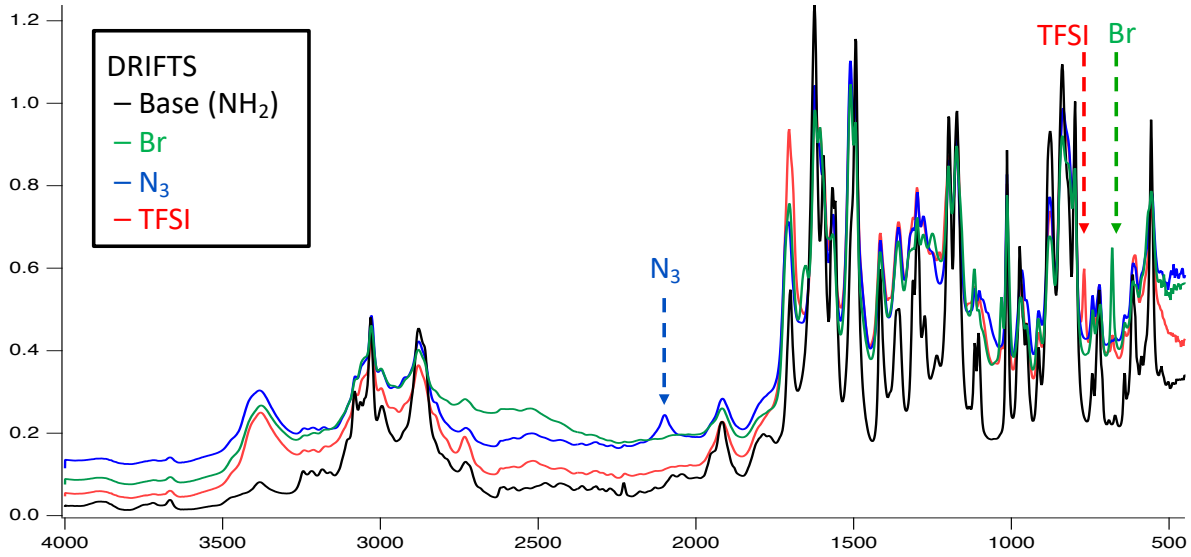




Accomplishment: Task 3 D Investigation of adsorbents as hydrogen carriers. (Porous liquids)

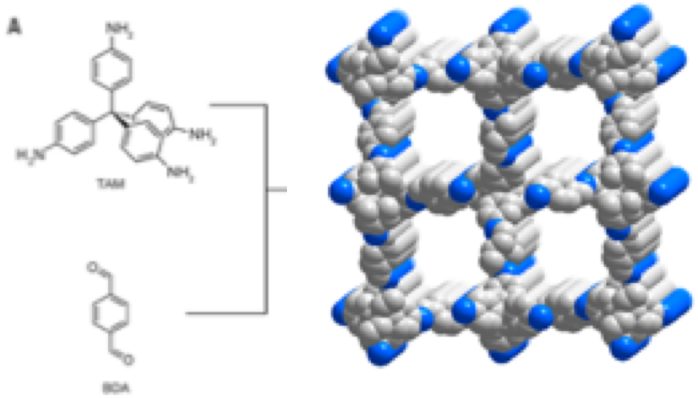
Confirmation of Click-Chemistry Reaction



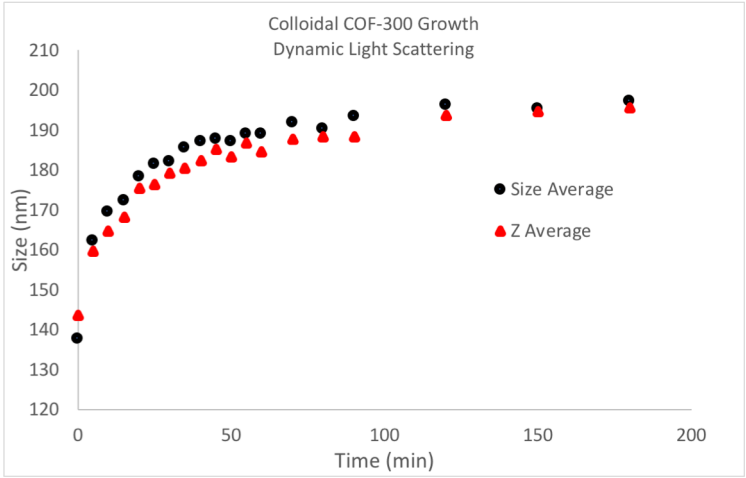


- DRIFTS results support that the click-chemistry synthesis was successful.
- Broadening of amine N-H stretch indicates chemical interaction.
- N_3 and C-Br stretches are only present in the relevant samples.
- New peaks (dashed lines) formed with the addition of TFSI are attributable to TFSI.
- **MILESTONE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

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



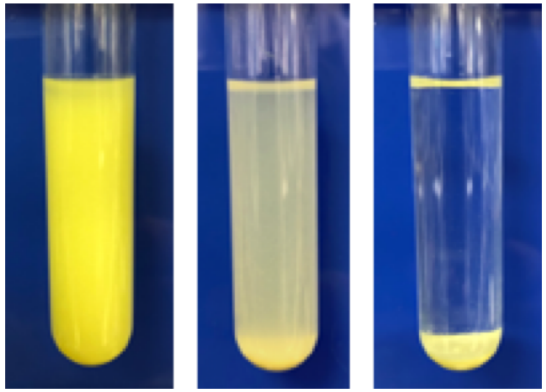
COF-300



Traditional Synthesis > 10 μm particles

Colloidal Synthesis, DLS vs time data

Suspension in CH_3CN

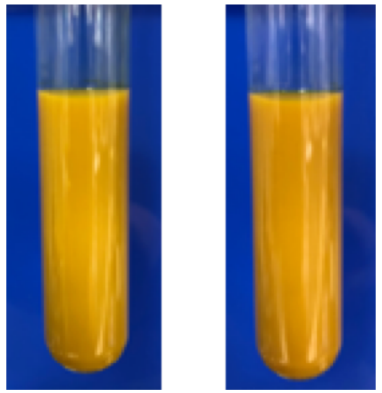


T_0 *1 h* *24 h*

Successful synthesis of small particles and colloidal suspension

TPD and "frozen" PCT are underway

Suspension in CH_3CN



T_0 *1 week*

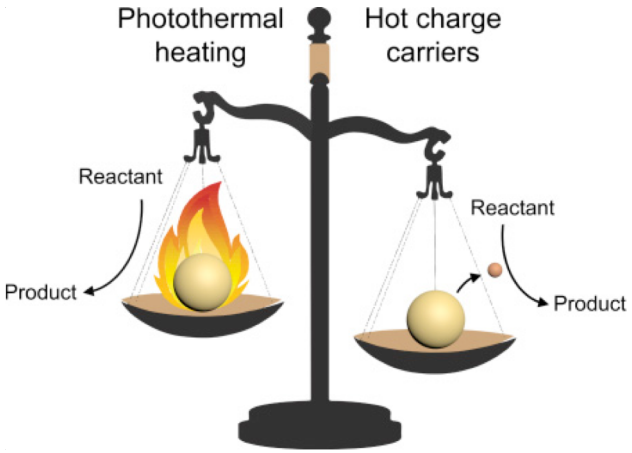
< 200 nm

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

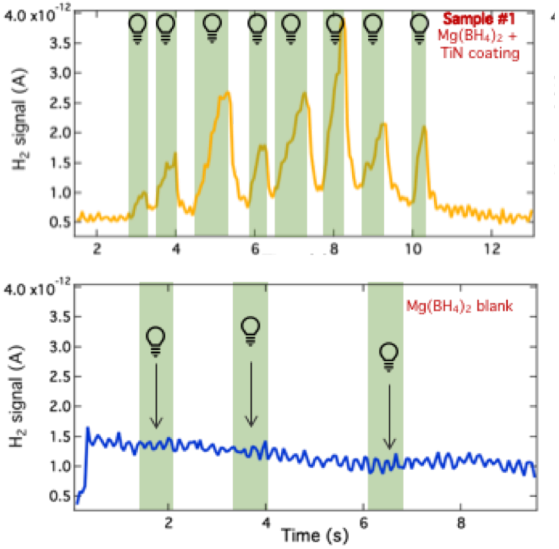


Utilize low energy light source to induce hydrogen sorption/desorption reactions and phase changes thermally and/or electrochemically

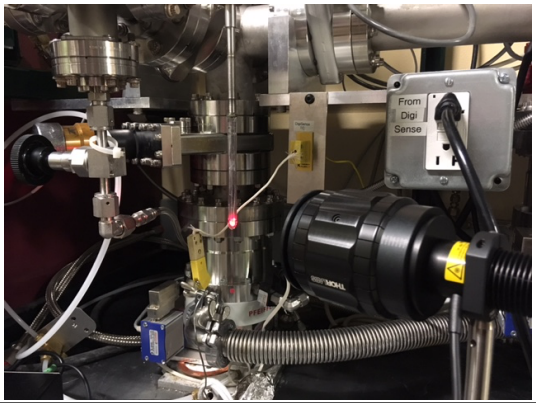
Pix from: https://www.differ.nl/vacancies/internship-nea

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

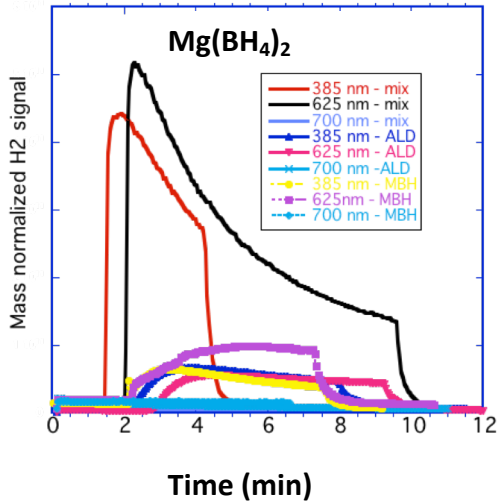
Preliminary Indications:

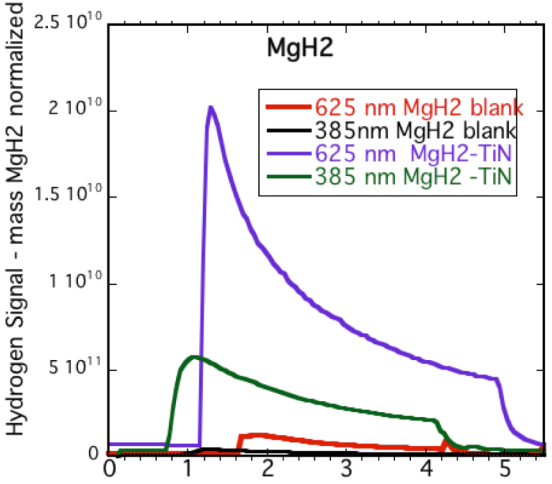
Non-optimized

625 nm – thermal degradation

385 nm – electrochemical reaction

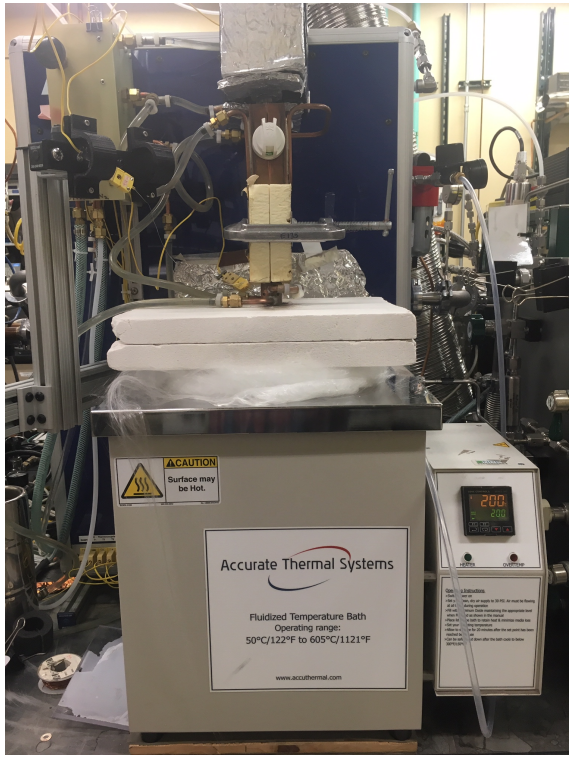
Dual illumination and *in-situ* studies underway

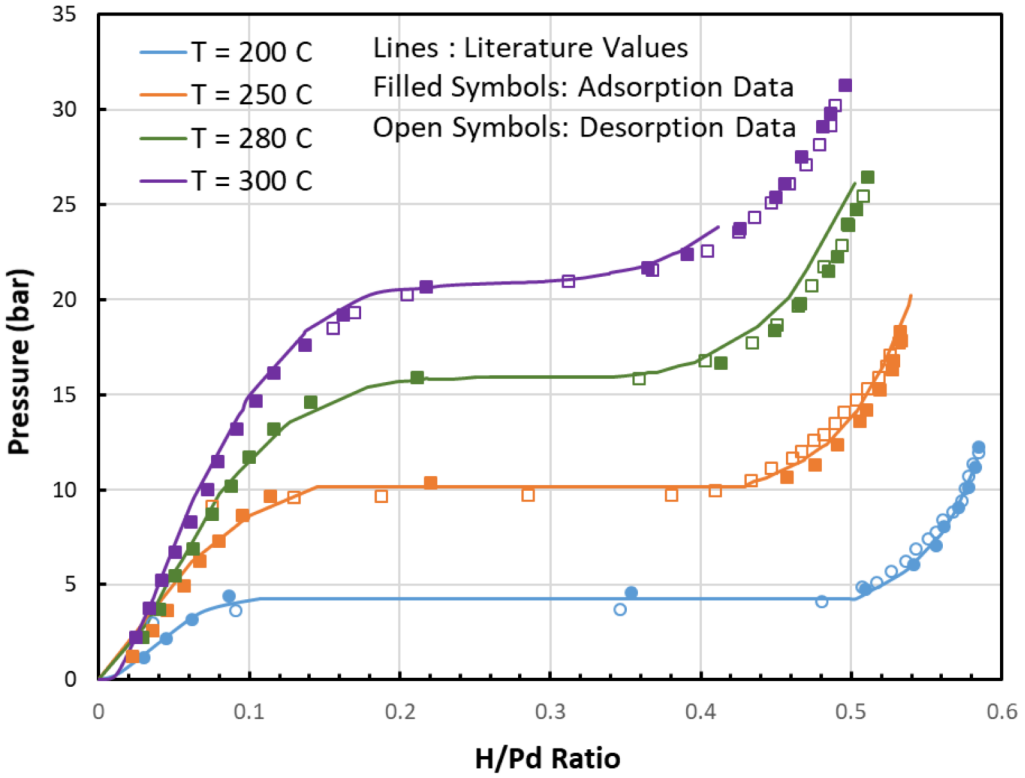




Accomplishment: Task 4a,High temperature validated PCT system

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





Accomplishment: Task 4 SLAC capabilities

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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NREL
NATIONAL RENEWABLE ENERGY LABORATORY

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 <u>interpretation</u>?**

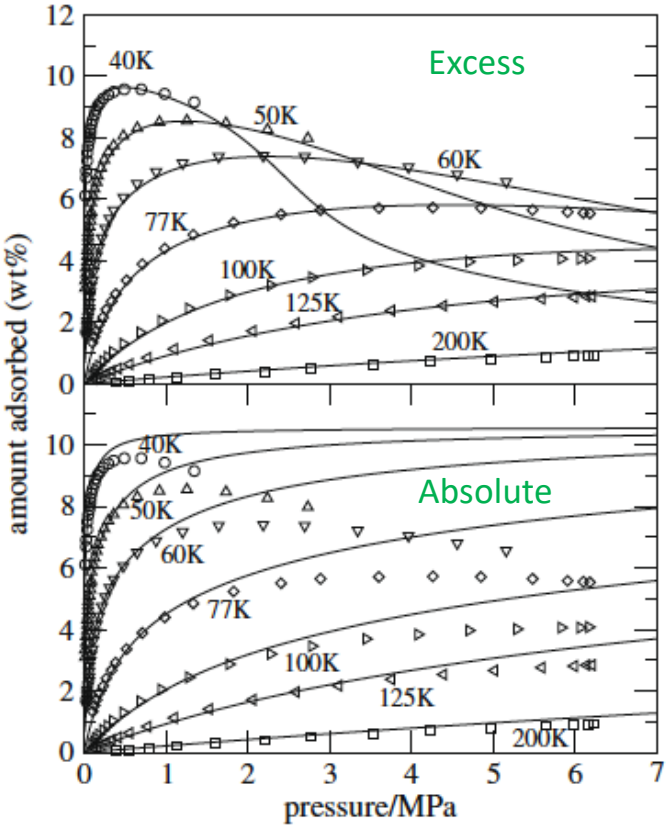
Assumptions:
ideal gas & adsorbed specific volume is negligible.

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

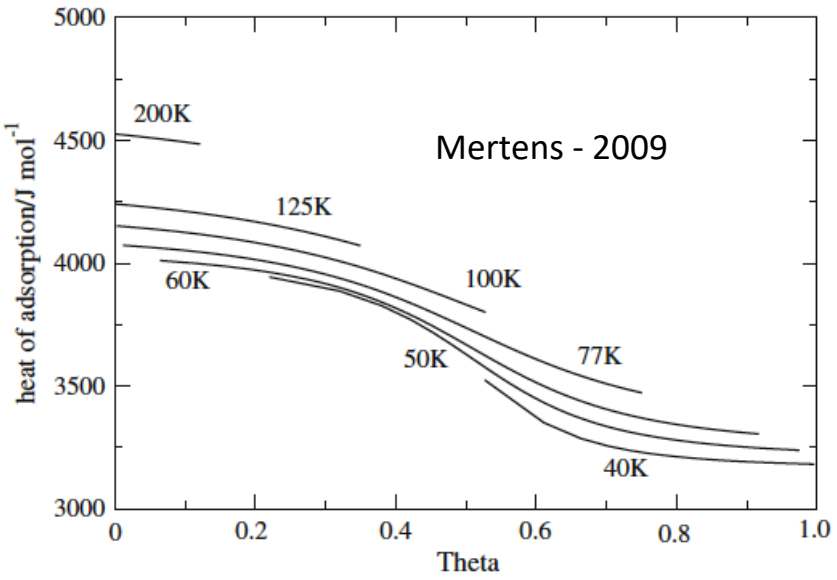
Determination of absolute adsorption in highly ordered porous media

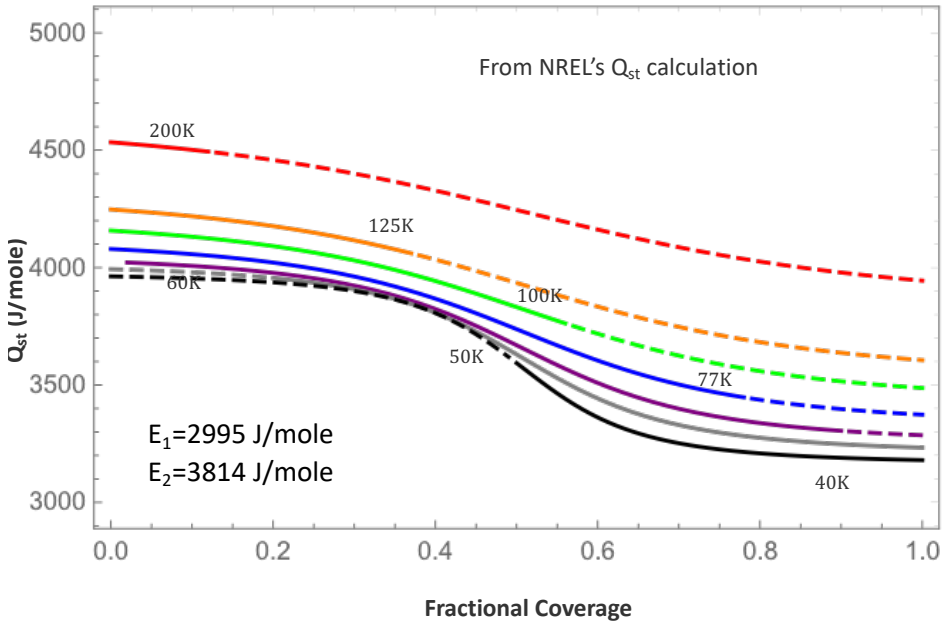
Florian O. Mertens * Surface Science 603 (2009) 1979–1984

- **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}

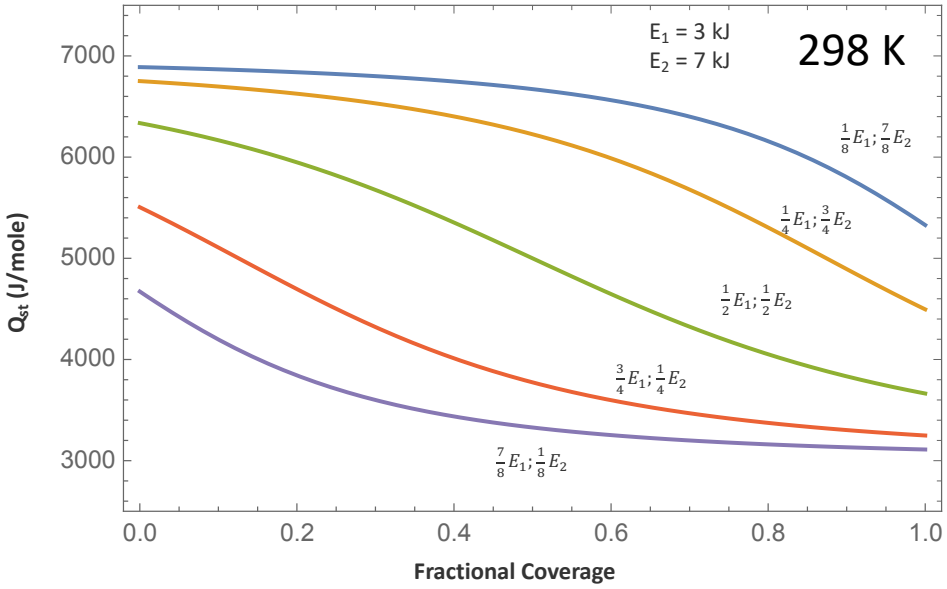


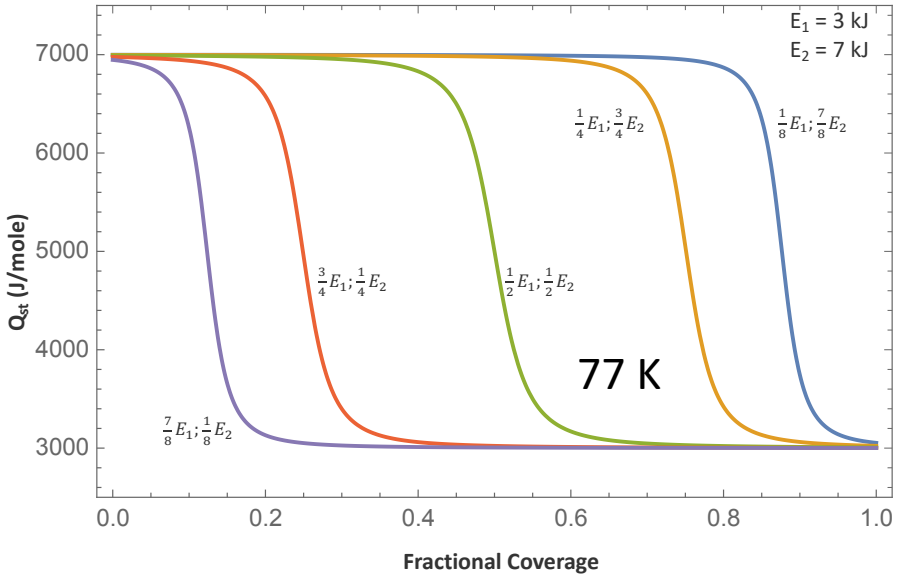


- **Mertens & NREL results are nominally identical.**
- ***Q_{st}* interpretation:**
  - Mertens interprets that Q_{st} changes with temperature & coverage
  - NREL isotherm modeling shows this interpretation is wrong and is an artifact of the initial choice of the isotherm fit
  - Instead there is intrinsic 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