HyMARC Core Activity: Characterization

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

Philip Parilla and David Prendergast

COVID-19 Pandemic halted all work in February 2020. Milestones to be evaluated after re-opening.

NREL NATIONAL RENEWABLE ENERGY LABORATORY | Sandia National Laboratories | Lawrence Livermore National Laboratory | BERKELEY LAB | ALS ADVANCED LIGHT SOURCE | MOLECULAR FOUNDRY | Pacific Northwest NATIONAL LABORATORY | NIST | SLAC NATIONAL ACCELERATOR LABORATORY





Project ID #: ST205

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

DOE Budget (Entire HyMARC Team)
Total FY19: $4.3M
Total FY20 (Planned): $6.25M

SNL: $1.15M
NREL: $1.5M (covers NIST and SLAC)
PNNL: $1.1M
LLNL: $0.9M
LBNL (Long): $1.1M
LBNL (Prendergast) $0.5M

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, 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,
Univ. Hawaii – Craig Jensen, Godwin Severa
Université de Genève – Hans-Rudolf Hagemann, Angelina Gigante

HyMARC Energy Materials Network: enhanced, highly coordinated capabilities to accelerate materials discovery

Enabling twice the energy density for hydrogen storage

- **Foundational R&D**
- **Computational models**
- **Synthetic protocols**
- **Advanced characterization tools**
- **Validation of material performance**
- **Guidance to FOA projects**
- **Database development**

Seedling Projects

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

Collaboration & Coordination: Seedling

Seedlings: the HyMARC team assists individual projects with:

- **A designated HyMARC point-of-contact**
- **Technical expertise concerning specific scientific problems**
- **Access to HyMARC capabilities**

Ongoing

- ***Development of Magnesium Boride Etherates as Hydrogen Storage Materials*** (U. Hawaii)
- ***Electrolyte Assisted Hydrogen Storage Reactions*** (Liox Power)
- ***ALD Synthesis of Novel Nanostructured Metal Borohydrides*** (NREL)
- ***Optimized Hydrogen Adsorbents via Machine Learning & Crystal Engineering*** (U. MI)

New

- *Optimal Adsorbents for Low-Cost Storage of Natural Gas and Hydrogen: Computational Identification, Experimental Demonstration, and System-Level Projection, U Mi*
- *Developing A New Natural Gas Super-Absorbent Polymer (NG-SAP) for A Practical NG Storage System with Low Pressure, Ambient Temperature, and High Energy Density, PSU*
- *Heteroatom-Modified and Compacted Zeolite-Templated Carbons for Gas Storage, MoSU*
- *Theory-Guided Design and Discovery of Materials for Reversible Methane and Hydrogen Storage, Northwestern Methane and Hydrogen Storage with Porous Cage-Based Composite Materials, UD*
- *Uniting Theory and Experiment to Deliver Flexible MOFs for Superior Methane or Hydrogen Storage, USF*
- *Metal-Organic Frameworks Containing Frustrated Lewis Pairs for Hydrogen Storage at Ambient Temperature USF*
- *Hydrogen Release from Concentrated Media with Reusable Catalysts, USC*
- *A Reversible Liquid Hydrogen Carrier System Based on Ammonium Formate and Captured CO2, WSU*
- *High Capacity Step-Shaped Hydrogen Adsorption in Robust, Pore-Gating Zeolitic Imidazolate Frameworks, Mines*
- *Development of Magnesium Borane Containing Solutions of Furans and Pyrroles as Reversible Liquid Hydrogen Carriers, UH*

Relevance: Hydrogen Storage Challenges

- The significant challenges associated with practical and economical hydrogen storage and transport require a *collaborative* national research effort among the leading *experts* and *shared capabilities*
- There are a myriad of plausible strategies for improving hydrogen-storage technologies that need to be investigated using state-of-the-art characterization
- The goal is to *Double* hydrogen storage energy density (increase from 25 to 50 g/L)

Relevance: NREL Characterization Activities

- Validate hydrogen capacity claims for DOE
  - Measure "champion" samples from DOE grant awardees
- Promote valid comparisons of hydrogen-storage materials and decrease irreproducibility due to errors
  - Provide uniform and well-defined metrics for comparisons
  - Understand sources of common errors and how to mitigate them
  - Promote volumetric capacity protocols
- Conduct inter-laboratory comparison for capacity measurements
  - Analyze actual implementations of protocols and variations thereof
  - Provide feedback to participants on errors and discrepancies
- Provide variable-temperature PCT measurements
- Provide *in-situ* thermal conductivity measurements
- Provide TPD & DRIFTS measurements

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

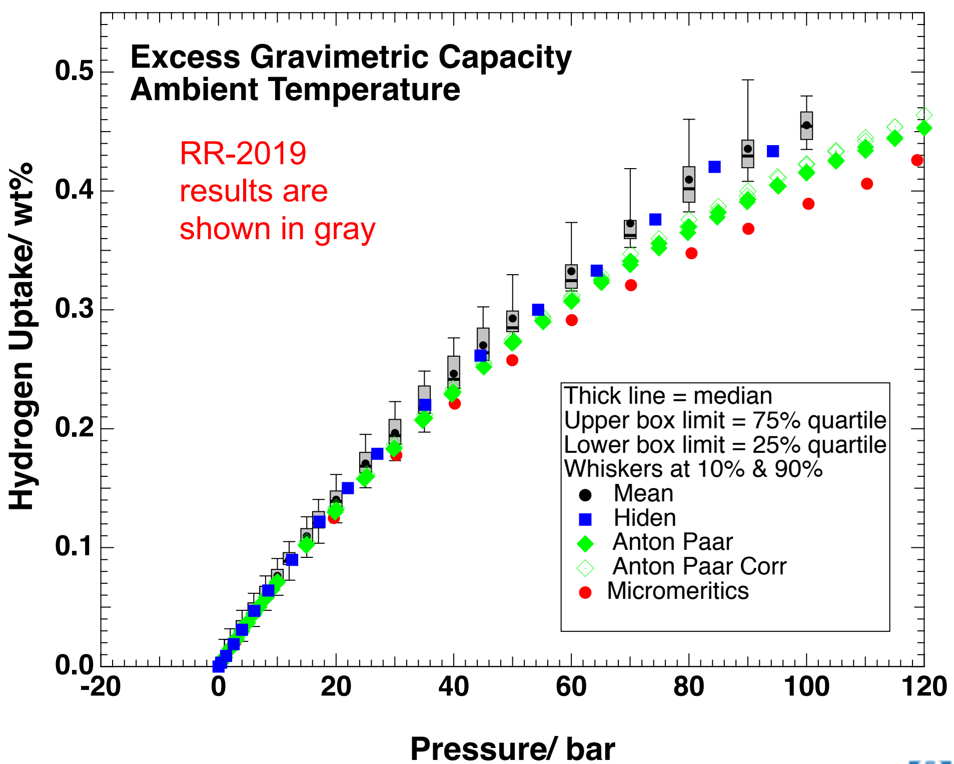
HyMARC

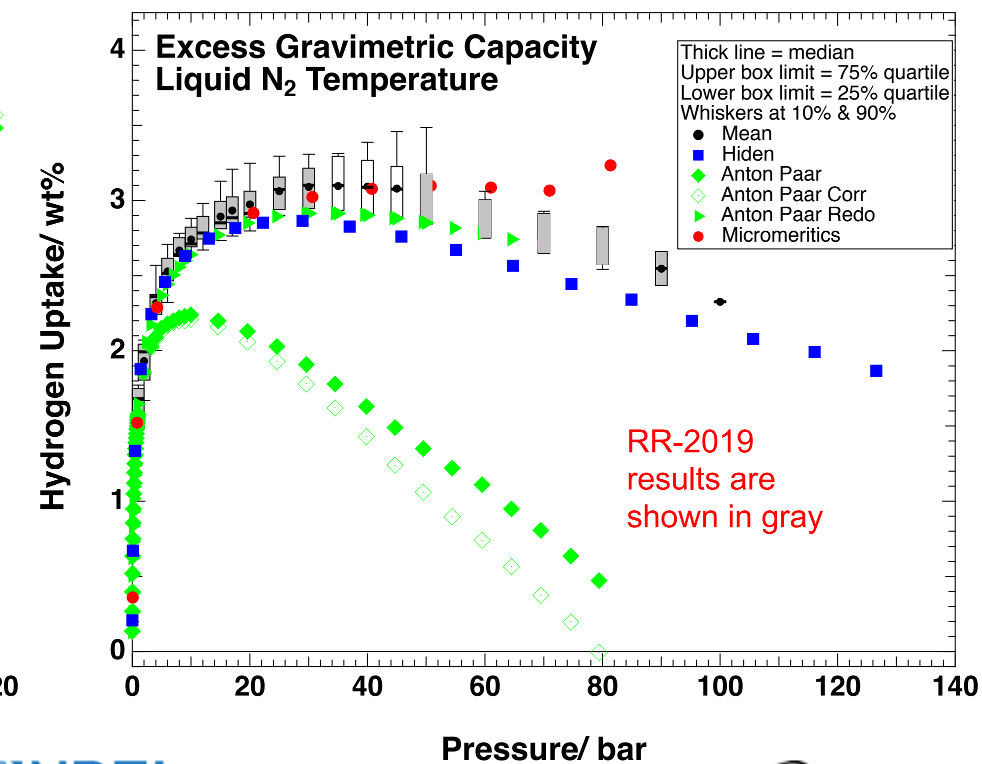
Approach: NREL Characterization Activities

- New PCT Evaluation
  - Review of quality for commercial PCT instrumentation
- Improvements to CryoPCT
  - Better temperature control & minimized residual torsion on sample holder
- Progress on Q_{st} Analysis
  - Additional analysis & publish paper
- Protocol development for expansive materials
  - How is capacity determination affected?
- DRIFTS & Synchrotron measurements
  - Seedling support
- Thermal Conductivity measurements
- Variable-temperature PCT measurements
- TPD & DRIFTS measurements

NREL Characterization Accomplishments

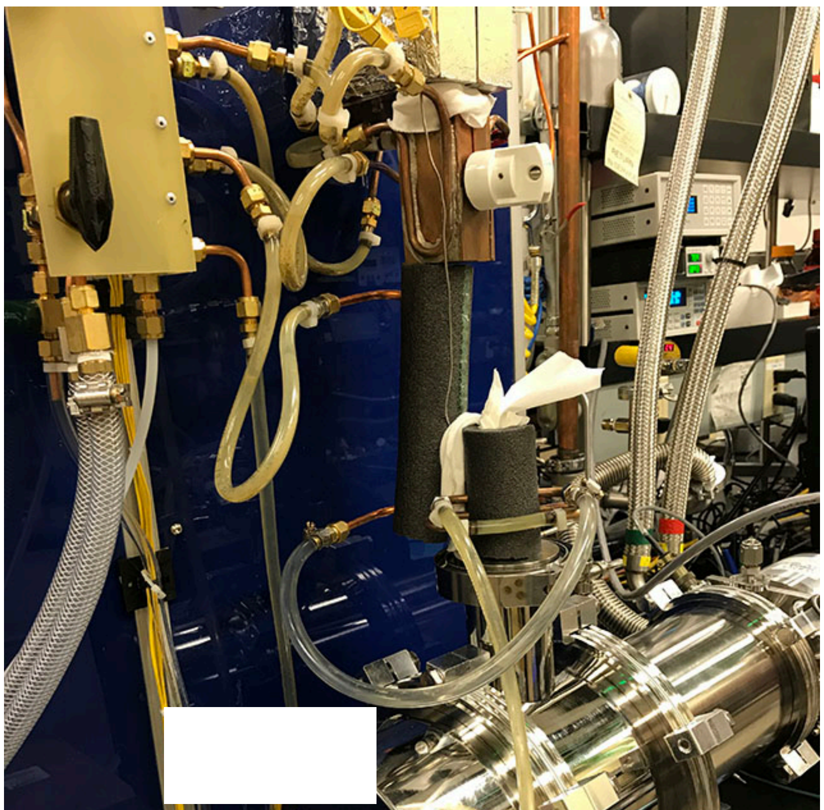
- **New PCT Evaluation**
  - Extensive investigation into current PCT instruments
  - Four main OEM: Setaram, Micromeritics, Anton Paar, Hiden
  - Mole-balance models, null measurements, & RR sample
  - Significant instrumental and operator issues for RR measurements
  - Setaram did NOT participate in RR sample (do not have testing capabilities)

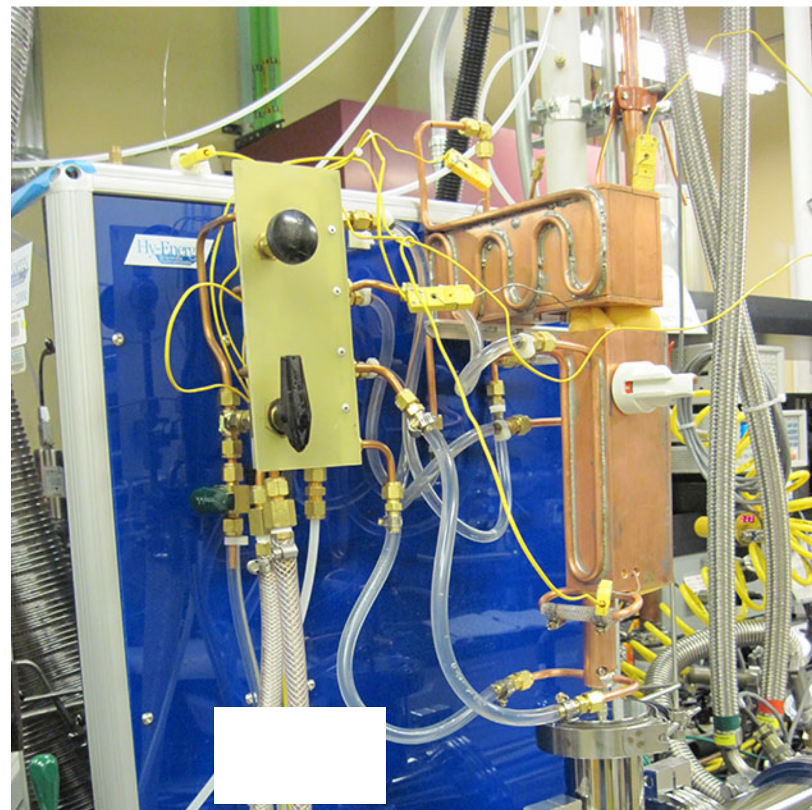




NREL Characterization Accomplishments

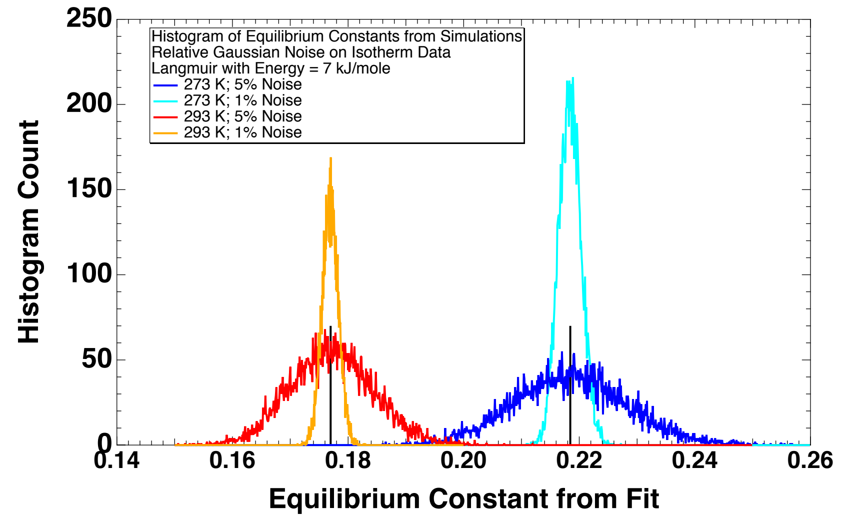
- **Improvements to CryoPCT**
  - Hardware modifications allow:
    - More uniform, stable, and reproducible temperature profiles
    - Minimizes residual torsional stress on sample holder
  - Master Calibrations are in Progress

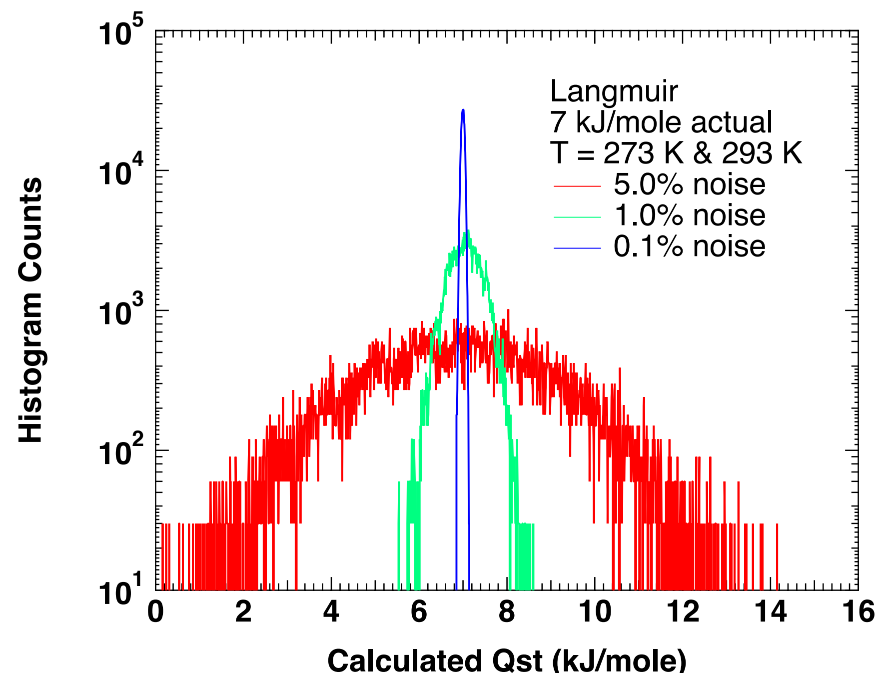




Progress on Isosteric Heat Analysis: Noise Sensitivity

- This data is generated from an idealized Langmuir model with Q_{st} = 7 kJ/mole at 273 & 293 K.
- Various noise levels added to the isotherms cause fits to the isotherms to not have the true values.
- Using these imperfect fits to determine Q_{st} then cause errors in Q_{st}.
- In this example, for a given noise level 'σ%', the resulting noise % level in Q_{st} is ~6nσ, where n is the # of std. dev.
- For σ=5% noise, it is quite probable to get 60% error in Q_{st} (n=2).





Advanced Characterization @ LBNL

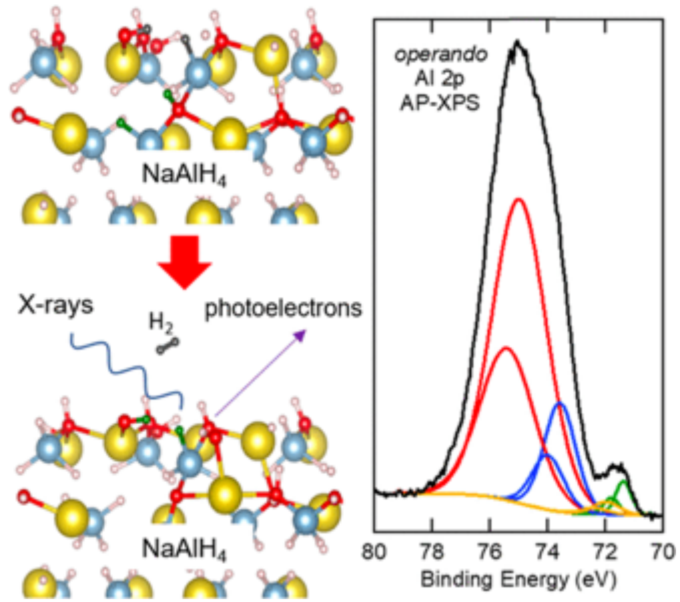
Sandia Contributors: White, El Gabaly
Stavila, Allendorf

Synchrotron AP-XPS
ALS BL 11.0.2

Lab-based AP-XPS
Sandia

Ambient Pressure XPS (Sandia)

Interpretation of near-surface XPS



White et al., ACS Appl. Mater. Interfaces ***11****, 4930 (2019)*

LLNL Collaborators:
Rowberg, Wan,
Kang, **Wood**

Advanced Characterization @ LBNL

In situ/Operando Soft X-ray Spectroscopy

Yi-Sheng Liu
Jinghua Guo

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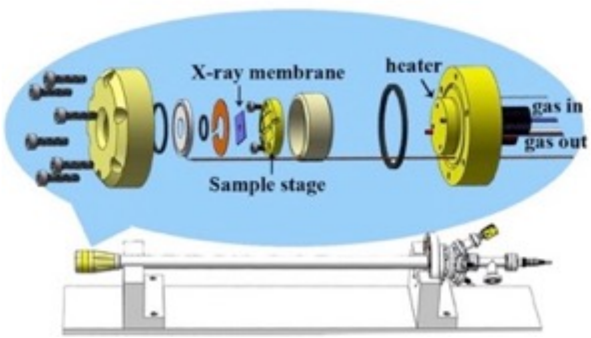
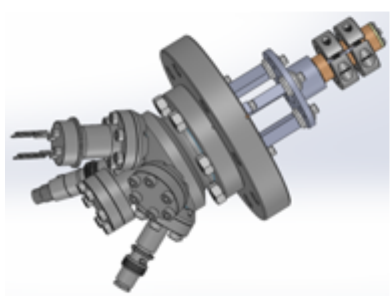


hydrogenation 1bar, RT- 250° C
TFY (um), TEY (nm)



H_2 release, RT- 500° C
TFY (um), TEY (nm)

Simulation of Interfaces and their X-ray Spectra

Pragya Verma
David Prendergast

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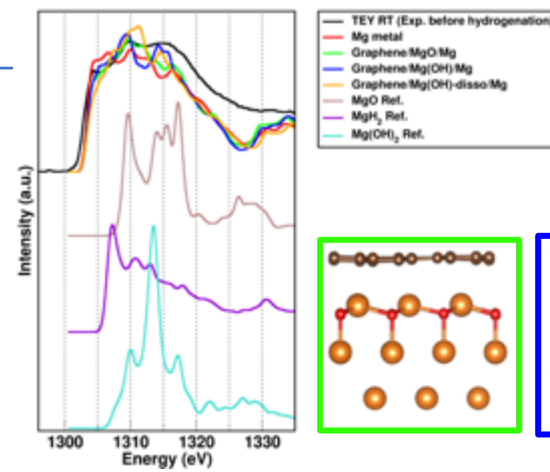
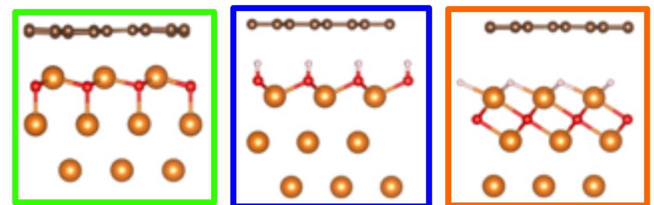
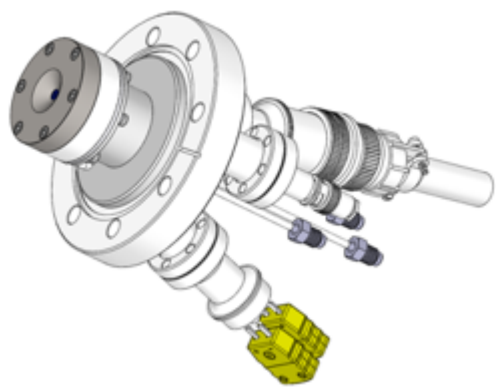
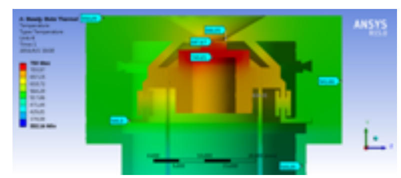






New H_2 reaction cell for soft x-rays:
- *H2 pressure: up to 5 bar*

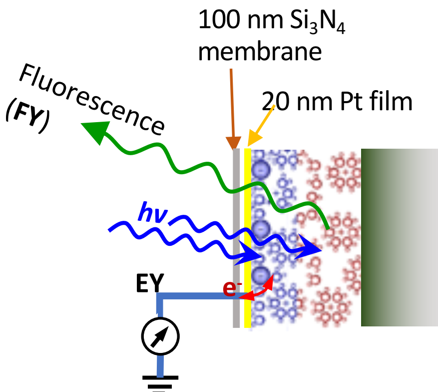


750 K

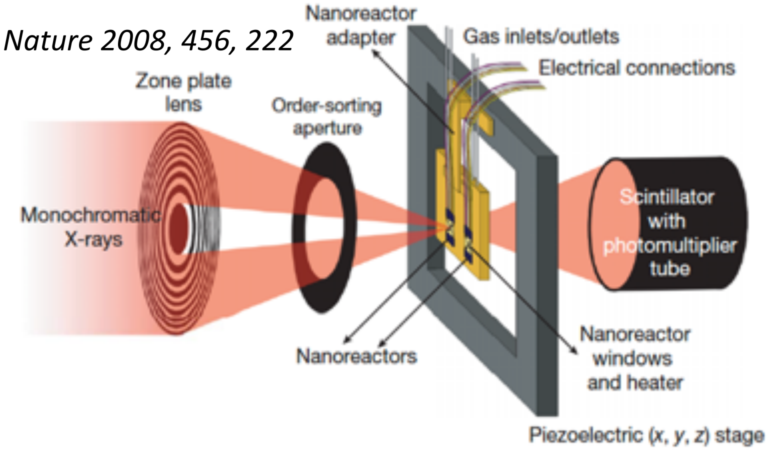
1000 K

Operando Soft X-Ray Characterization Techniques

Yi-Sheng Liu
Jinghua Guo

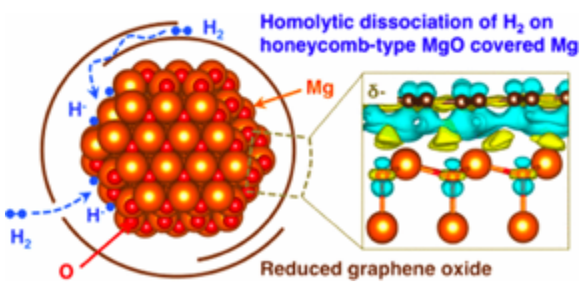


Nature 2008, 456, 222



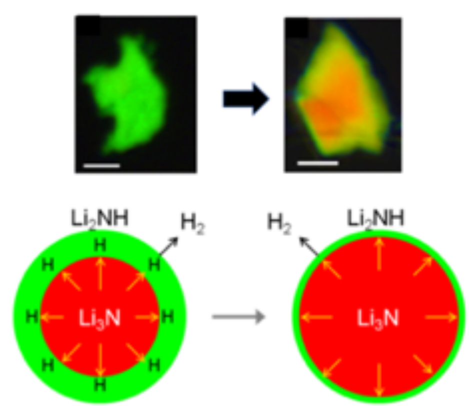
Operando XAS/RIXS

Knowledge of the structure and composition of nanometer-thin solid-gas interface regions is key for understanding H_2-adsorption/-desorption phenomena



Operando STXM

Microscopy platform for imaging nanoscale changes inside hydride particles, which provides new insights about performance and adsorption/desorption that could improve hydrogen storage



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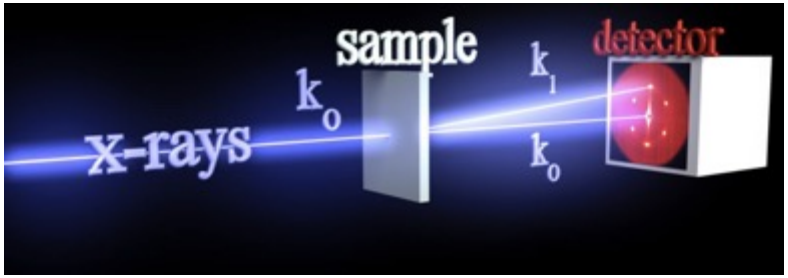
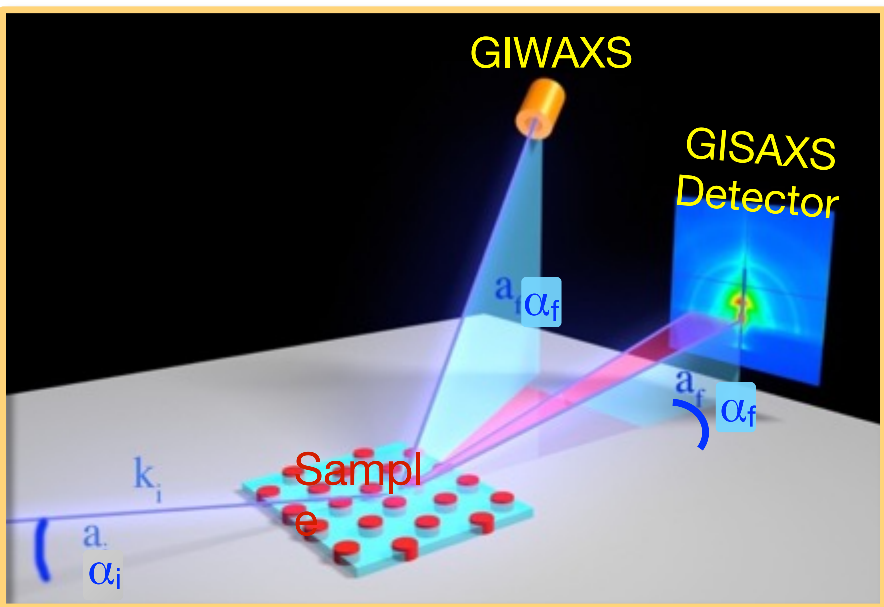
Structure characterization capabilities

Yi-Sheng Liu
Jinghua Guo

Transmission SAXS/WAXS

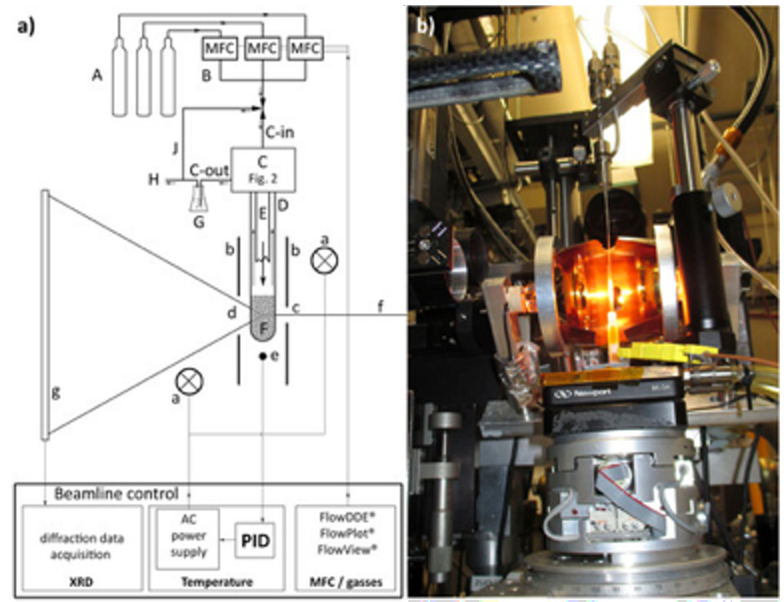


Grazing incidence SAXS/WAXS



thin films on substrate
(20 - 100 nm thick)

In situ and *operando* high temperature X-ray powder diffraction in variable gaseous environments



- Temperatures in excess of 1100° C, controlled ramp rates in excess of 100° C/min
- Controlled gas environments from mTorr to ~2atm
- In-situ and in-operando time resolved studies

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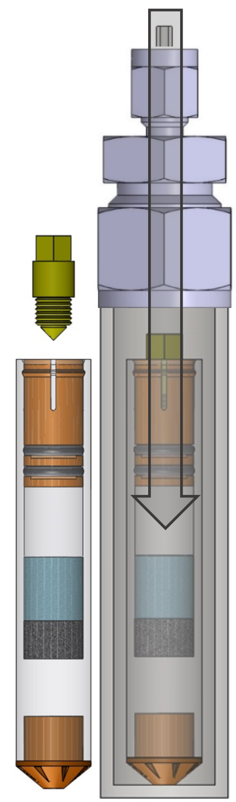
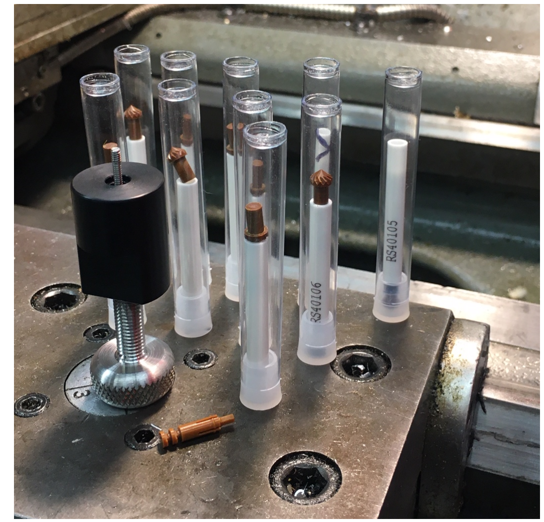
Advanced Characterization Capabilities (4.C: NMR Spectroscopy)

High Pressure NMR Capability

- New rotors for high pressure NMR
  - 1-way valve for sequential addition of gas to sealed rotor
  - 200 bar pressure
  - -20 to + 50 °C, greater temperature range being developed
  - Static or magic-angle spinning
  - Greater control of sample inside detection coils
- 10 rotors prepared for HyMARC researchers to load at their laboratories
  - Minimizes contamination during loading
  - Toolset for loading and unloading can be distributed





Design of rotors to allow 1-way gas addition (left); and rotors and tools under construction in the EMSL workshop (top).

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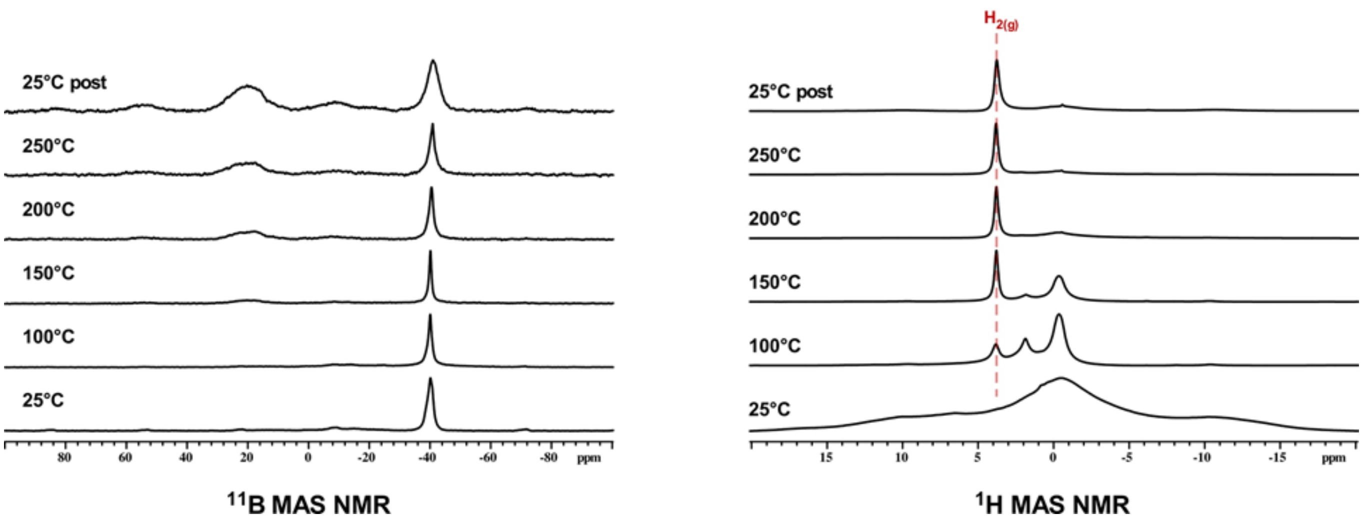
Advanced Characterization Capabilities (4.C: NMR Spectroscopy)

Seedling Support: MAS-NMR of ALD-coated $Mg(BH_4)_2$

- Use of high-pressure NMR rotors to study dehydrogenation *in situ* of $Mg(BH_4)_2$ coated with BN, TiN
- H_2 observed at 100 °C when using “wet” N_2H_4 in the ALD process (not “dry”)
- New boron signal at ca. +20 ppm correlated with H_2 generation
  - Strongest for 10 BN /100 TiN layers

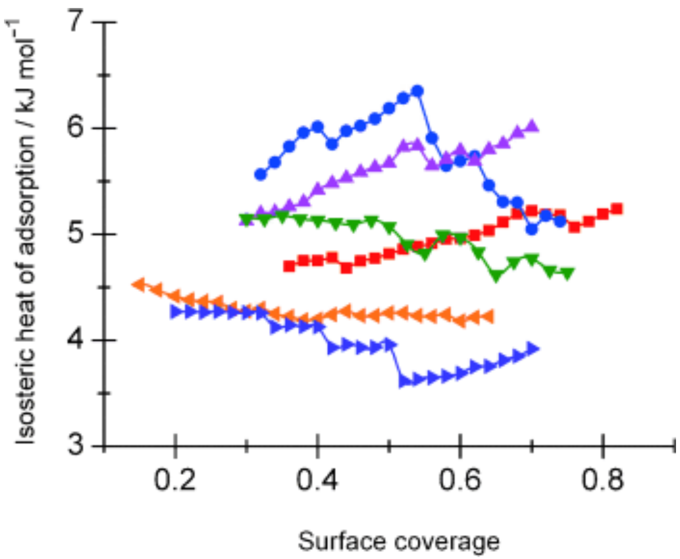
γ-$Mg(BH_4)_2$ 10 cycles of BN & 100 cycles of TiN



Noemi Leick - NREL

Advanced Characterization Capabilities (4.B: PCT CALORIMETRY)

Simultaneous determination of the adsorption isotherm and the adsorption enthalpy



- We are developing a microcalorimetric setup capable of measuring isotherm and enthalpy directly at sub-ambient conditions
- Currently differential enthalpy calculated using Clausius–Clapeyron equation
- Combining a low temperature Calvet-Tian calorimeter with a PCT as a microdoser
- Capable of measuring adsorption isotherm and enthalpy at 77K and above

Low Temperature Calorimeter (from -196° C to 200° C (BT2.15)

References:
L. Llewellyn et al., C. R. Chimie 8 (2005).
JA Mason et al. Nature 1-15 (2015) doi:10.1038/nature15732
B. Schmitz et al, ChemPhysChem, Volume 9, Issue 15, pages 2181–2184 (2008)

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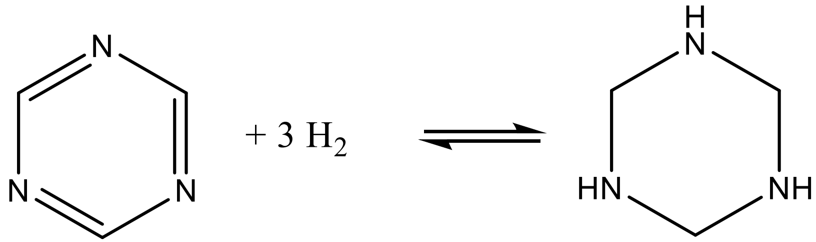
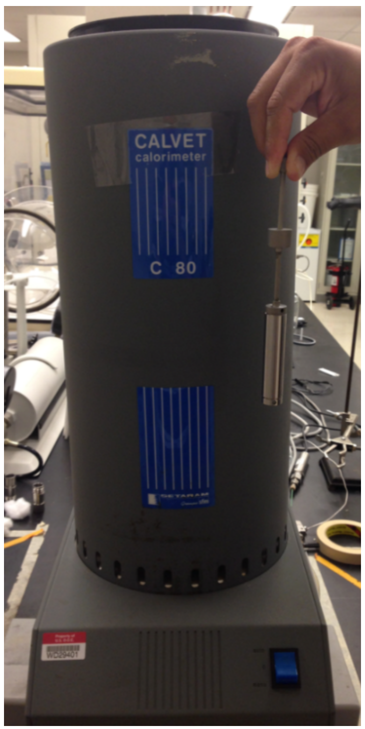
Reaction calorimetry: direct measure of heat of triazine hydrogenation



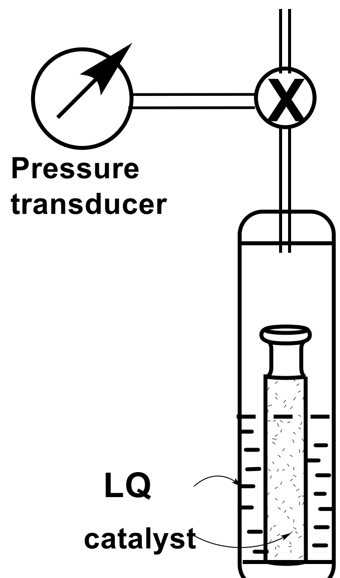
+ heat

s-triazene

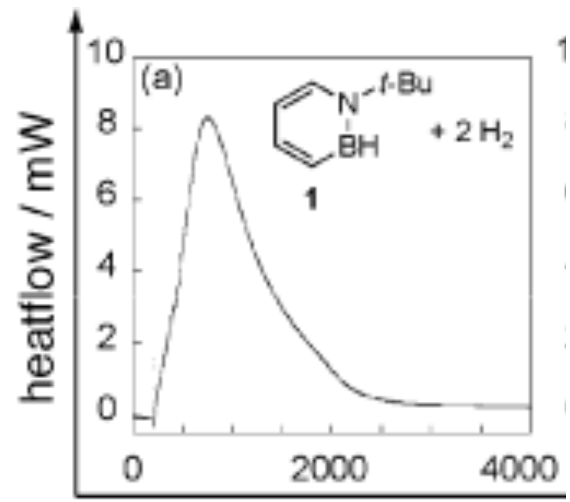
perhydro-triazene



First experiments. Measurement of enthalpy of H_2 uptake by triazine. ΔH =36 or 54 kJ/mol H_2?



Campbell, Abbey, Neiner, Grant, Dixon, Liu
J. AM. CHEM. SOC. 2010, *132*, 18048



Heat of hydrogenation of CBN

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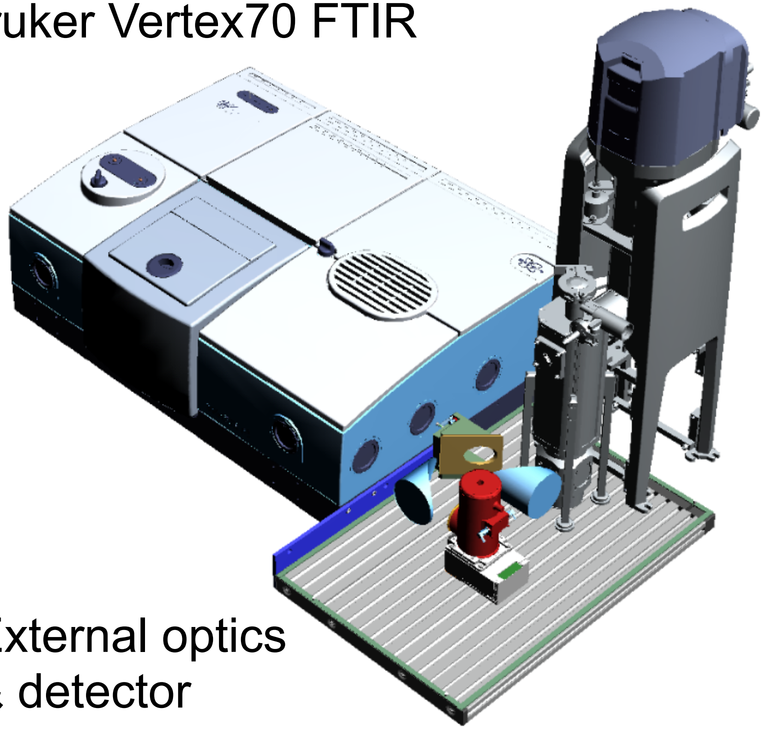
New Spectrometer Design

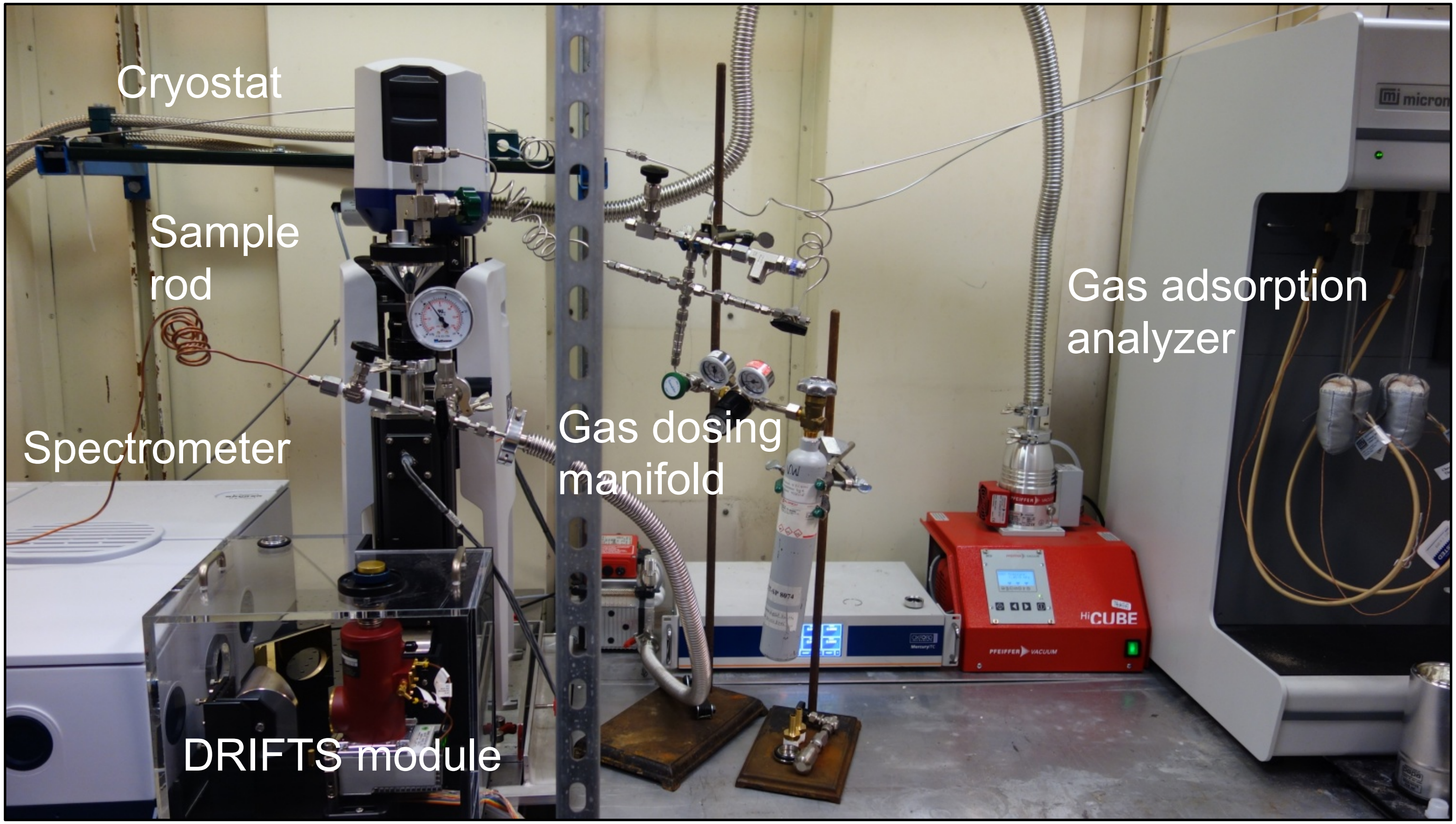


Spectrometer	
Range (MCT)	8,000–650 cm^{-1}
Resolution	0.4 cm^{-1}
Temperature Control	
High Temperature Cell	35–180 °C
Low Temperature Cell	300–15 K
Pressure Control	
ASAP2020Plus	0–1 bar
HPVA II*	0–120 bar

* Coming soon

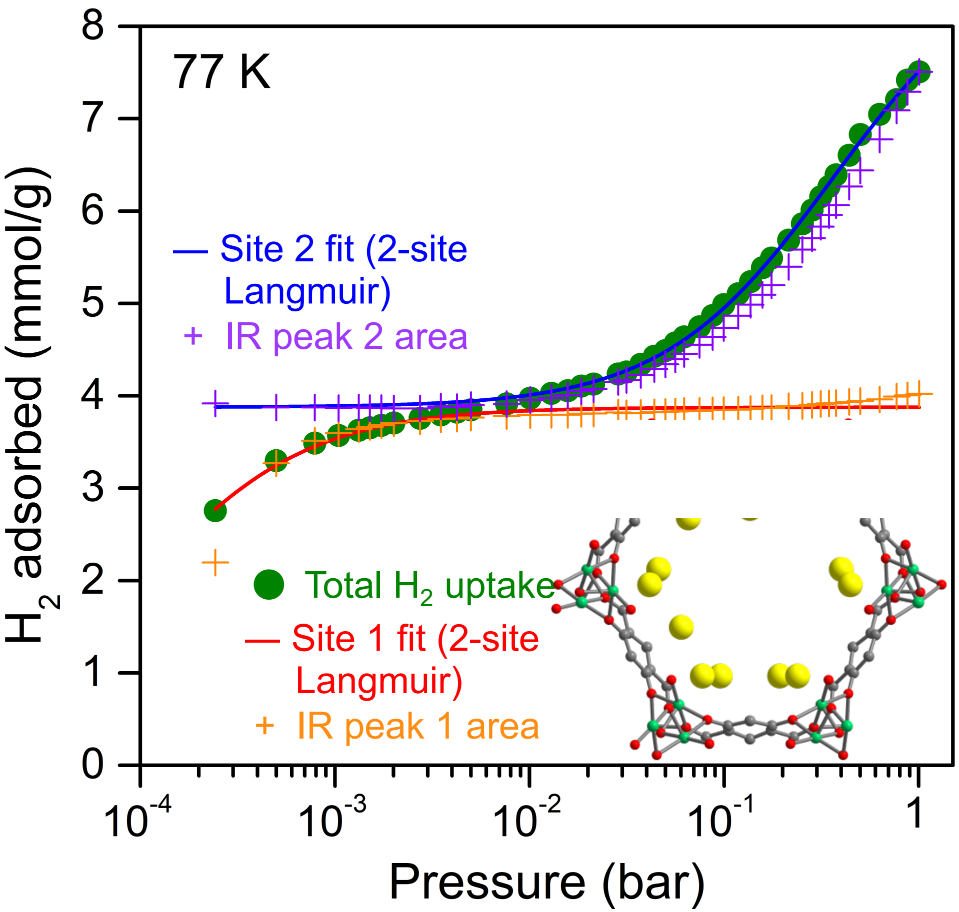
- Custom design improving on previous setups
- External optical path allows modularity
- Many different temperature/pressure options available

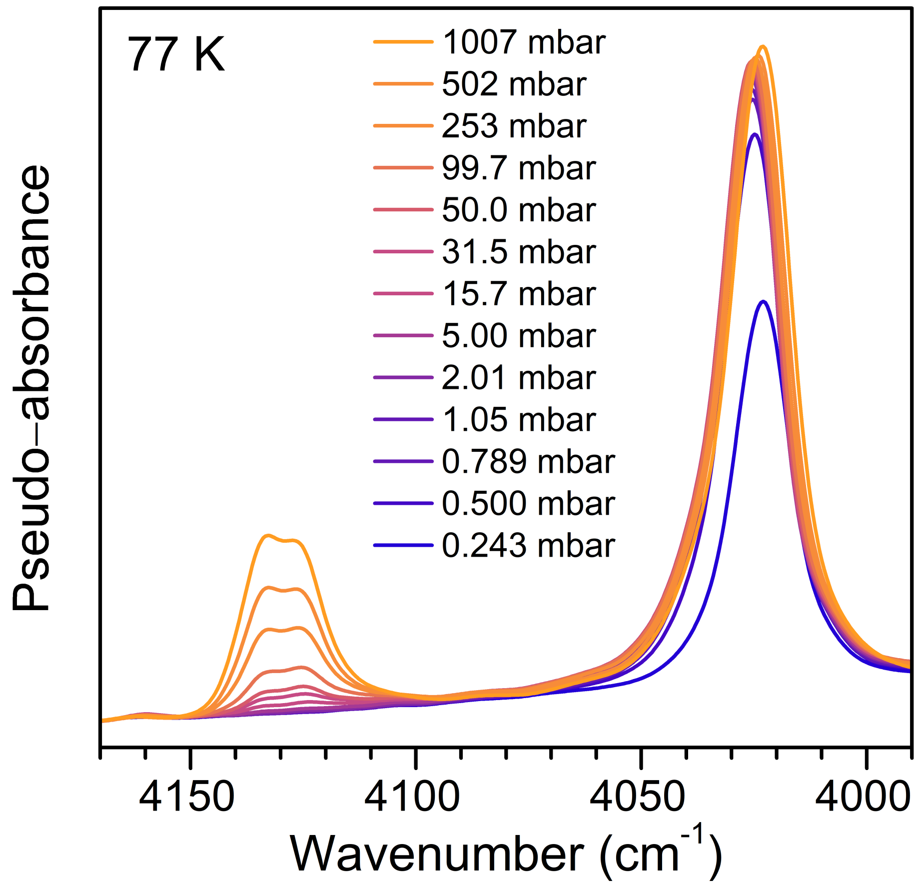
In Situ Gas Dosing Variable Temperature FTIR



- Custom design improving on previous setups
- External optical path allows modularity
- Many different temperature/pressure options available

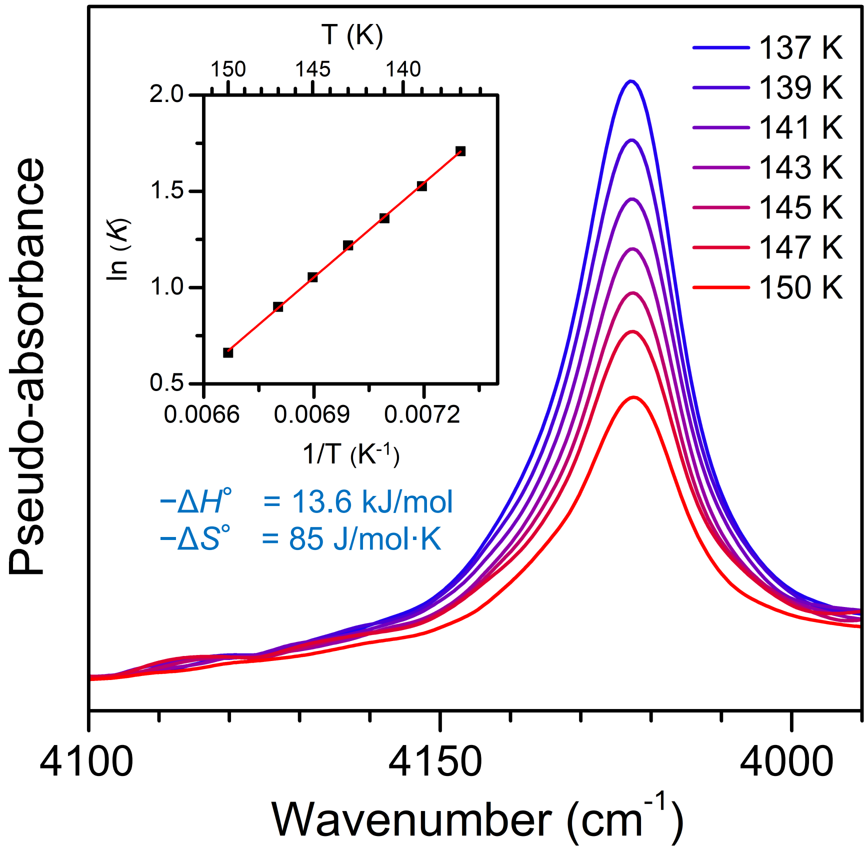
Tracking Individual Adsorption Sites

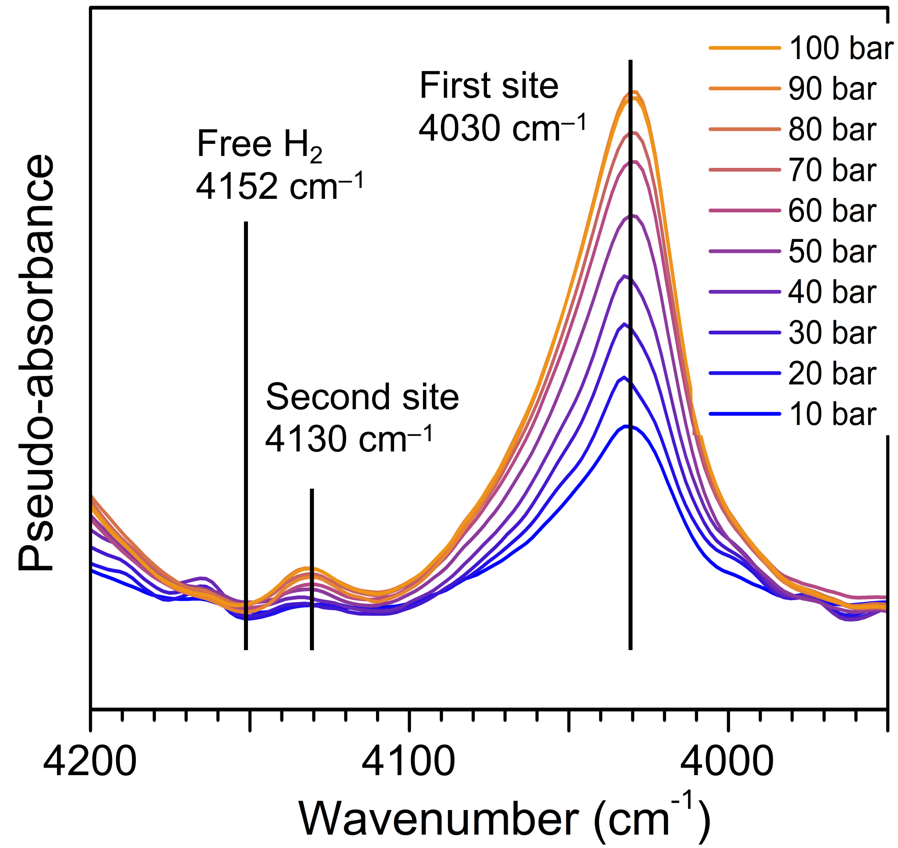




- Integrating area under IR peak allows site-specific quantification

Variable Temperature & High-Pressure IR



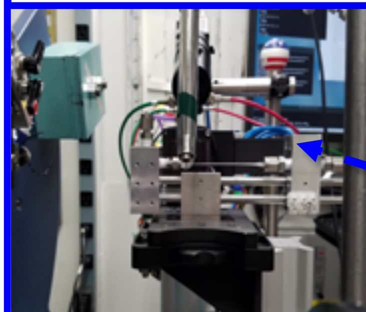


- Van't Hoff relation allows determination of site-specific thermodynamics
- Comparable with zero coverage Q_{st}
- Manifold was pressurised with H_2 up to 100 bar and both sites observed at higher pressures

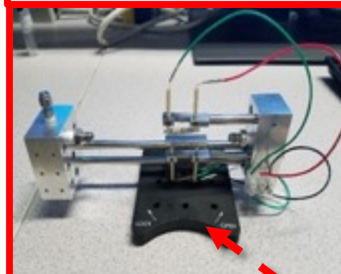
BERKELEY LAB

R&D of Advanced Characterization Core Capabilities at SLAC

Oxford Cryostream:
90 – 298 K



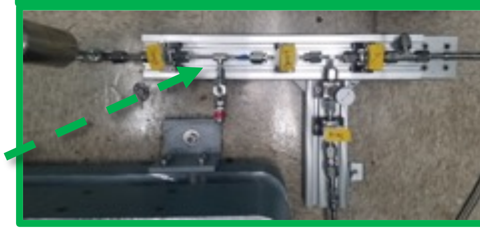
Nichrome Heaters:
20–800° C



Next steps:
Design and 3D print "dark cell" enclosure for pulsed optical experiments
(HyMARC plasmon projects)

Pressure-resolved measurements

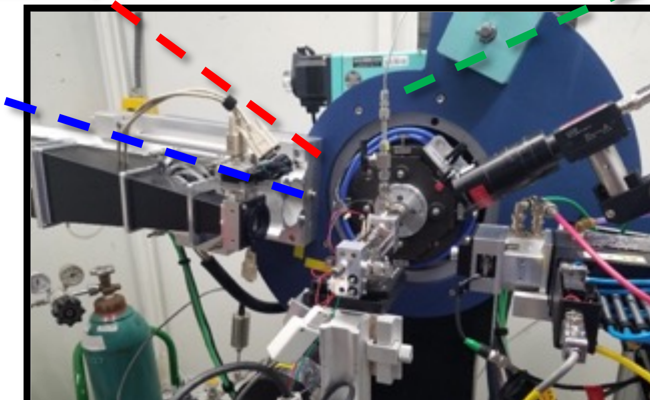
NREL Variable Pressure Gas Manifold:
P_{max} = ~100 bar, P_{min} = ~10^{-7} mbar



Static or variable pressure option

Heating option

Cooling option



Capillary sample cell mounted at SSRL BL 2-1

Anton Paar DHS 900 domed hot stage (i.e. flat plate geometry) also available

Currently in progress:
New sample cell mounted in CCR with gas dosing capabilities, lower T_{min} to ~10 K
(HyMARC sorbent projects)

Next steps:
Interfacing PCT system with the in-situ scattering cell
(HyMARC sorbent, hydrides projects)

➢ Capillary sample holder options:
- High-purity quartz, 0.2 mm thick T_{melt}= ~1700° C, P_{max} = ~130 bar @ RT)
- Single crystal sapphire, 0.4mm thick T_{melt} = ~2300° C, P_{max} = ~550 bar@RT)
- Kapton (polyimide)

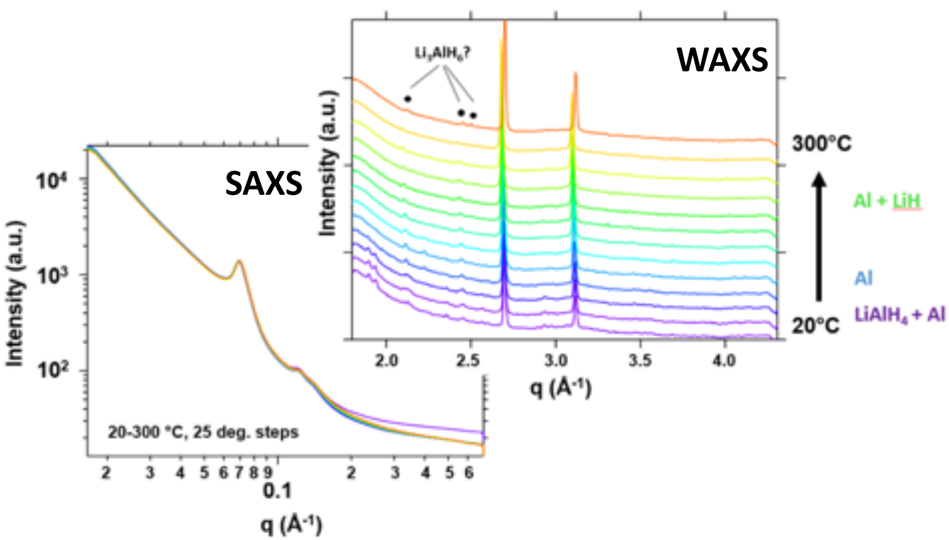
Compatible with a variety of techniques
- X-ray diffraction (XRD)
- Small angle x-ray scattering (SAXS)
- X-ray pair distribution function analysis (PDF)
- X-ray Raman spectroscopy (XRS)
- X-ray absorption spectroscopy (XAS)

SLAC NATIONAL ACCELERATOR LABORATORY
Nicholas Allan Strange
Michael Toney

R&D of Advanced Characterization Core Capabilities at SLAC

Hydrides: FA 2.D.2 Non-innocent hosts for MH encapsulation (SNL – Stavila)

SAXS suggests the LAH and N-CMK_3 domains remain fixed in size with increasing temperature. N-doping appears to potentially stabilize a reversible intermediate



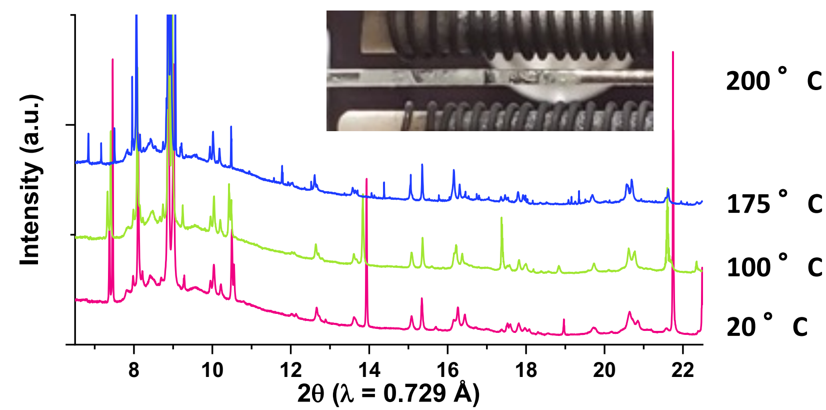
SAXS/WAXS on $LiAlH_4$ nanoconfined in N-doped CMK-3 mesoporous carbon

Hydrogen Carriers: FA 3.C Eutectic Systems and Hydrogen Carriers (NREL – Bell)

β-$Mg(BH_4)_2$ + $(CH_3)_4NBH_4$

Physical mixture results in new phase (possible eutectic) formation around ~175° C

Phase melts around 200° C and migrates away from heat source (see inset)



Sandia National Laboratories

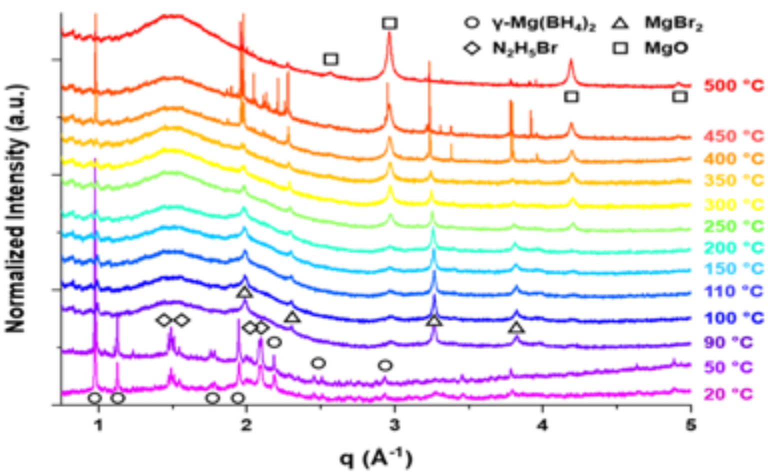
SLAC NATIONAL ACCELERATOR LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

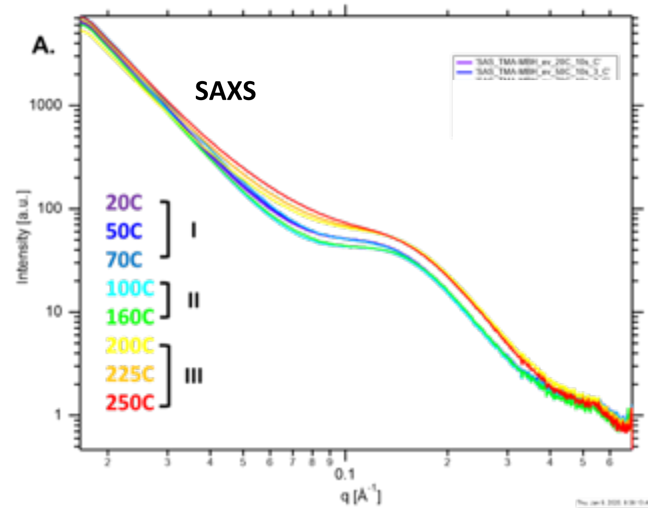
Research Support for HyMARC Seedling Support (NREL-Christensen)

100c N_2H_4 + BBr_3 on γ-$Mg(BH_4)_2$

Temperature-resolved XRD shows N_2H_5Br in the room temperature product. The hydrazinium species melts around 90° C shortly followed by formation of $MgBr_2$ and rapid H_2 release

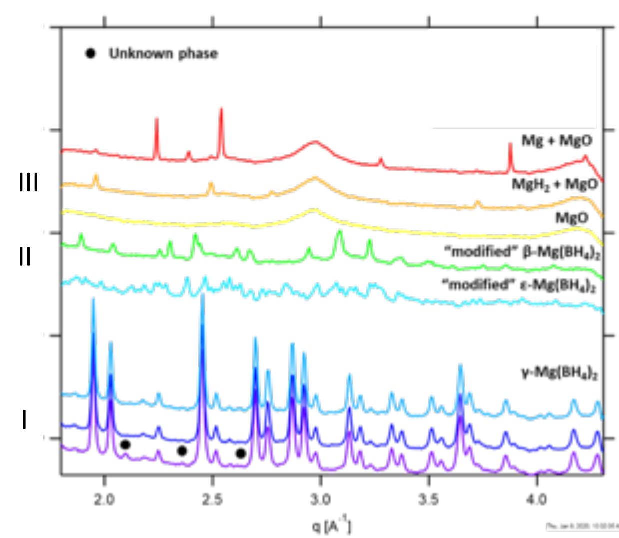


100c $Al_2(CH_3)_6$ on γ-$Mg(BH_4)_2$



In situ SAXS suggests the pore structure originating from γ-$Mg(BH_4)_2$ is retained with increasing temperature

WAXS



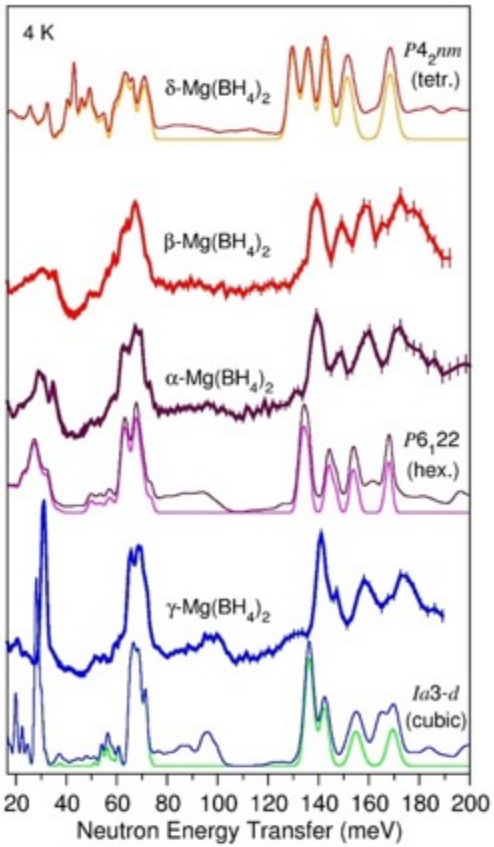
WAXS shows the TMA-MBH sample forms MgH_2 and Mg nearly 100 ° C lower than the neat borohydride

Nicholas Allan Strange
Michael Toney

SLAC NATIONAL ACCELERATOR LABORATORY
NREL NATIONAL RENEWABLE ENERGY LABORATORY

H_2 Storage Characterization and Optimization Research Effort

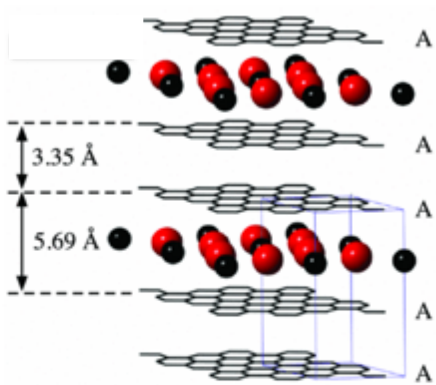
Craig Brown
Ryan Klein



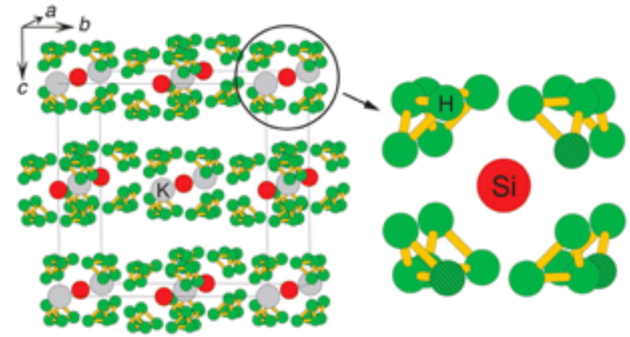
INS & DFT of $Mg(BH_4)_2$
Polymorphs (w\ SANDIA)

Chemically bound

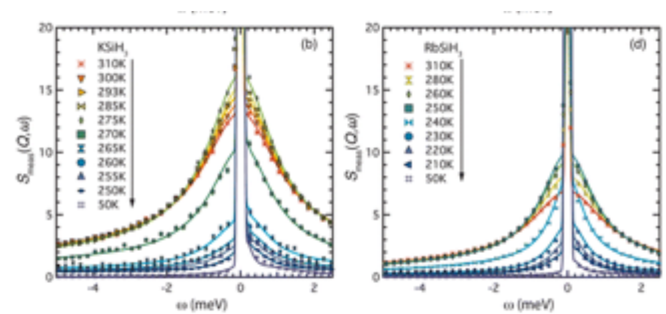
Provide information about
- *where the 'H' is*
- *How is it bound/adsorbed*
- *How it moves*

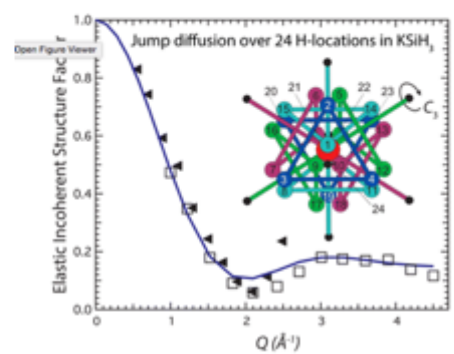


Molecular



Chemically bound





Proposed Future Work

- Assist the seedling projects by using HyMARC's unique characterization capabilities
- Apply the same characterization capabilities to HyMARC's internal materials-research programs
- Publish findings using state-of-the-art and unique characterization capabilities to investigate new hydrogen storage and carrier materials
- Develop new and improve existing characterization capabilities to enhance understanding and optimization of hydrogen storage and carrier materials

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

Summary

- The significant challenges associated with practical and economical hydrogen storage and transport require a collaborative national research effort among the leading experts and shared capabilities
- Many of these capabilities exist at national user facilities at ALS, NIST, PNNL, & SLAC
- Activities include these characterization capabilities:
  - Calorimetry
  - *In-situ* DRIFTS
  - *In-situ* FTIR
  - INS
  - *In-situ* NMR
  - PCT
  - PCT calorimetry
  - *In-situ* Thermal Conductivity
  - SAXS
  - *Operando* STXM
  - TPD
  - WAXS
  - XAS
  - *Operando* XPS
  - *In-situ* XRD
  - X-ray PDF
  - XRS

Contributors

- LBNL
  - J Guo
  - YS Liu
  - JR Long
  - P Verma
- LLNL
  - S Kang
  - AJE Rowberg
  - LF Wan
  - BC Wood
- NIST
  - CM Brown
  - RA Klein
- NREL
  - RT Bell
  - ST Christensen
  - T Gennett
  - KE Hurst
  - N Leick
  - R Mow
  - S Shulda
- PNNL
  - T Autrey
  - ME Bowden
  - K Grubel
  - AJ Karkamkar
- SLAC
  - NA Strange
  - MF Toney
- SNL
  - MD Allendorf
  - F El Gabaly
  - V Stavila
  - JL White

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HyMARC

Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

Tech Back Up Slides

A Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Temperature Programmed Desorption

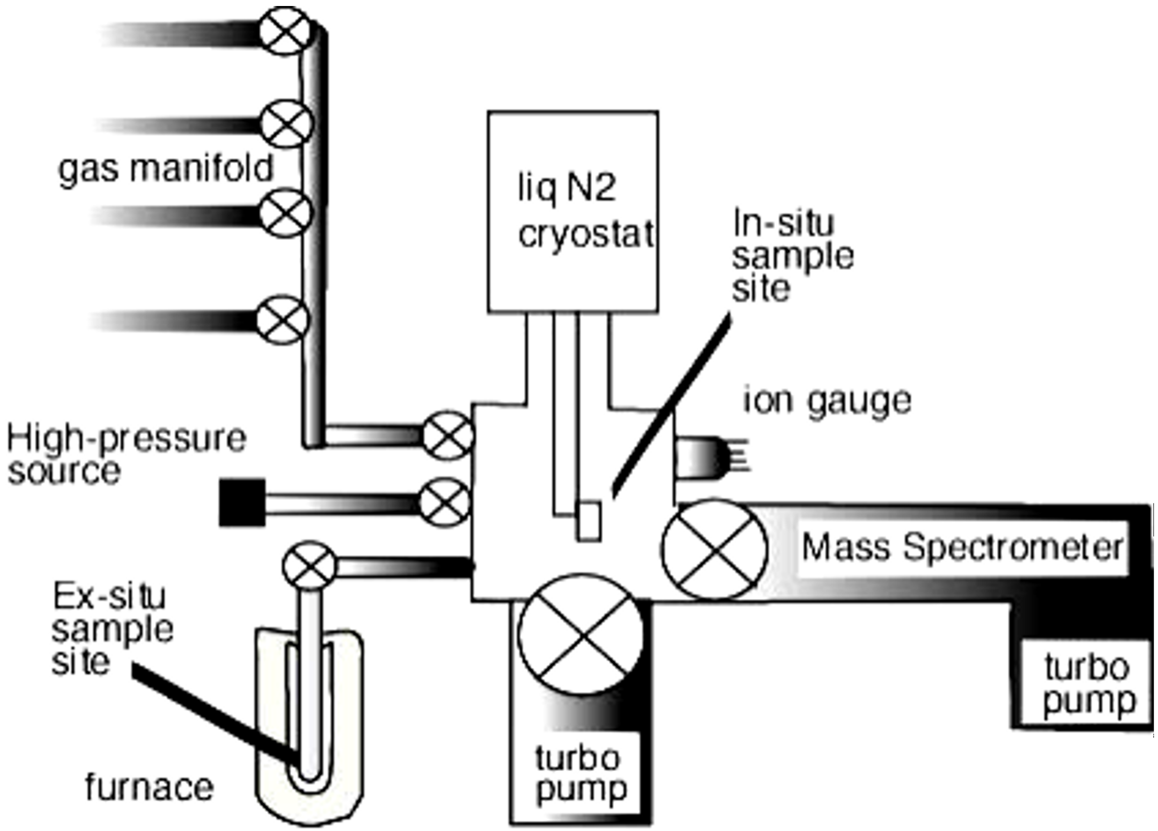


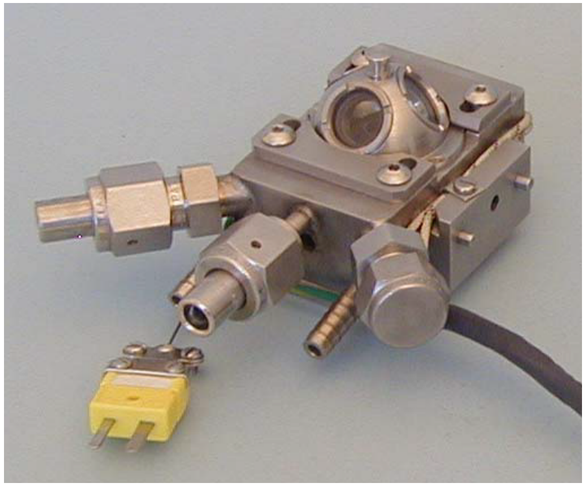
Diagram of TPD apparatus

- Sample is heated in high vacuum at a constant rate
- 77 K < T < 1500 K
- Molecular effluents are monitored vs T with the mass spec.
- Can detect any volatile adsorbed species
- Can be calibrated to measure H_2 capacity
- Provides activation energy and order of desorption

General Reference: R.J. Madix, Chemistry and Physics of Solid Surfaces, Volume II, ed. R. Vanselov, CRC, Boca Raton, (1979) 63-72

Cryo DRIFTS Capability

• *In-situ* DRIFTS



High temperature reaction chamber suitable for studies at controlled temperatures (up to 1183 K) and pressures (up to 34 bar)

- High pressure dome and ZnSe windows
- Three inlet/outlet ports for evacuating the cell and introducing gases

Low temperature reaction chamber suitable for studies at variable temperatures (123 K to 873 K) and pressures (up to 1.3 bar)

- Attached dewar cooled with liquid nitrogen

* Chambers are used in conjunction with the Praying Mantis diffuse reflectance accessory (Harrick)

DSC/TGA/MS/GC

- Simultaneous TG-DSC coupled with a mass-spec
- Additional capabilities to couple with FTIR or GC
- -150 to1000 °C temperature range with controlled atmosphere