HyMARC:
Technical Activities at SLAC

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DOE Hydrogen Fuel Cells Program

2019 Annual Merit Review and Peer Evaluation Meeting

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Project ID: st201

Overview

Timeline*

Phase 1: 10/1/15 to 9/30/18

Phase 2: 10/1/18 to 9/30/22

Budget

1 post-doc is provided for this effort through HyMARC/NREL

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, NREL

H_2ST^2, USA – Hydrogen Storage Tech Team

Colorado School of Mines - Colin Wolden, Brian Trewyn

Relevance: New Capabilities for HyMARC at SLAC

- Support research activities from core labs by providing access to advanced synchrotron x-ray characterization facilities

- Develop opportunities for using novel techniques which provide new information for complex processes
  - *e.g. resonant techniques, total scattering pair distribution function (PDF) analysis, x-ray Raman, x-ray reflectivity*

- Develop new sample cells for *in situ / ex situ* measurement capabilities (variation in temperature, pressure)
  - Capillary sample cell
  - Low-temperature (<77K) transmission sample cell

- Provide microscopic/macroscopic information to derive structure-property relationships

- Provide route for understanding structural evolution during dehydrogation and rehydrogenation (i.e. H_2 cycling) processes

Approach – Focus areas where SLAC offers support

Task 1. Sorbents
1.B Focus Area: Optimizing Sorbent Binding Energies
    1.B.2 Synthesis of sorbents with optimal binding energies
1.D Dynamic Sorbent Materials
    1.D.2 Thermal/photo-responsive sorbent matrices
1.F Focus Area: Nanoscale Defects in sorbents

Black – active
Red – future

Task 2. Hydrides
2.A Focus Area: MH Thermodynamics
    2.A.1 Phase Diagrams for ternary borohydrides
    2.A.3 Thermodynamics of complex metal hydride eutectic mixtures
2.B Focus Area: Solid Interfaces and Surfaces
    2.B.2 Experimental probing of surface and buried interface chemistry
2.C Focus Area: Activation of B-B and B-H Bonds
    2.C.1 Modulation of B-H bond strength in borohydrides
2.D Focus Area: Nanoscaling to improve thermodynamics and kinetics
    2.D.1 Nano-confined metal hydrides under mechanical stress
    2.D.2 Non-innocent hosts for MH nanoencapsulation
2.E Focus Area: Microstructural Impacts of CMH Hydrogenation / Dehydrogenation Reactions

Task 3. Hydrogen Carriers
3.C Focus Area: Eutectic Systems and Hydrogen Carriers
3.D Focus Area : Investigation of Adsorbents as Hydrogen Carriers
    3.D.2 Porous liquids as hydrogen carriers
3.G Heterolytic Cleavage and Activation of Hydrogen
    3.G.1 Frustrated Lewis acid -base pairs

Task 4: Research and Development of Advanced Characterization Core Capabilities
4.D Focus Area: Advanced *in-situ* and *ex-situ* Synchrotron and ATR/DRIFTS Characterization Techniques
    4.D.1 Diffraction
    4.D.2 Small Angle X-Ray Scattering
    4.D.3 XAS/EXAFS
    4.D.5 Ambient Pressure X-ray Photoelectron Spectroscopy

Accomplishments: Sample Cell Development

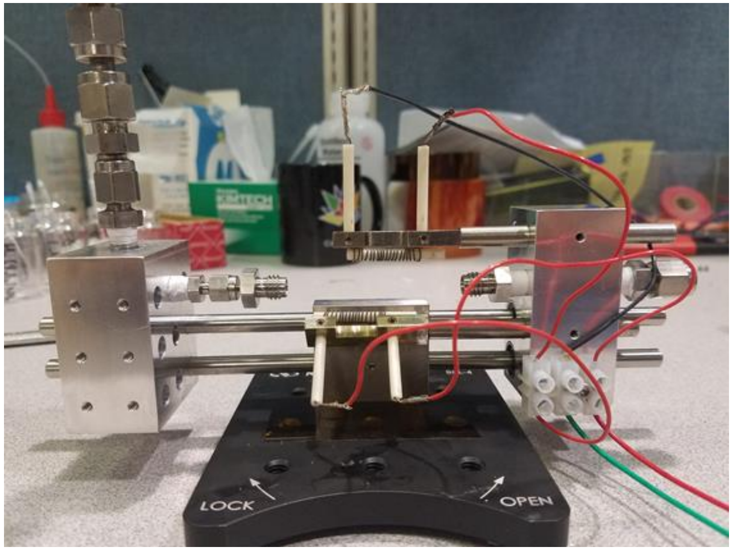
Ultimate objective is to provide/enhance in situ capability upper limits (T≥600°C, P≥100 bar) while optimizing signal quality for beamlines at SSRL

Thin-walled capillary sample cell – considerations in design:

Material selection: high-purity quartz (~100 bar), single crystal sapphire (100-300 bar)

Wall thickness: 10, 20, 100 μm (thicker for PDF @ APS)

Stability/reactivity of seal: Vespel/graphite ferrules, 5-min epoxy, Celvaseal, Torrseal



Versatile design – easily transferrable across multiple beamlines/techniques (XRD, PDF, and SAXS)

Currently existing model at SSRL uses the design of Hoffmann et al. *J. Synchrotron Rad.* (2019) 26

Accomplishments: *In Situ* X-Ray Diffraction (XRD) – SSRL BLs 2-1, 7-2, 10-2

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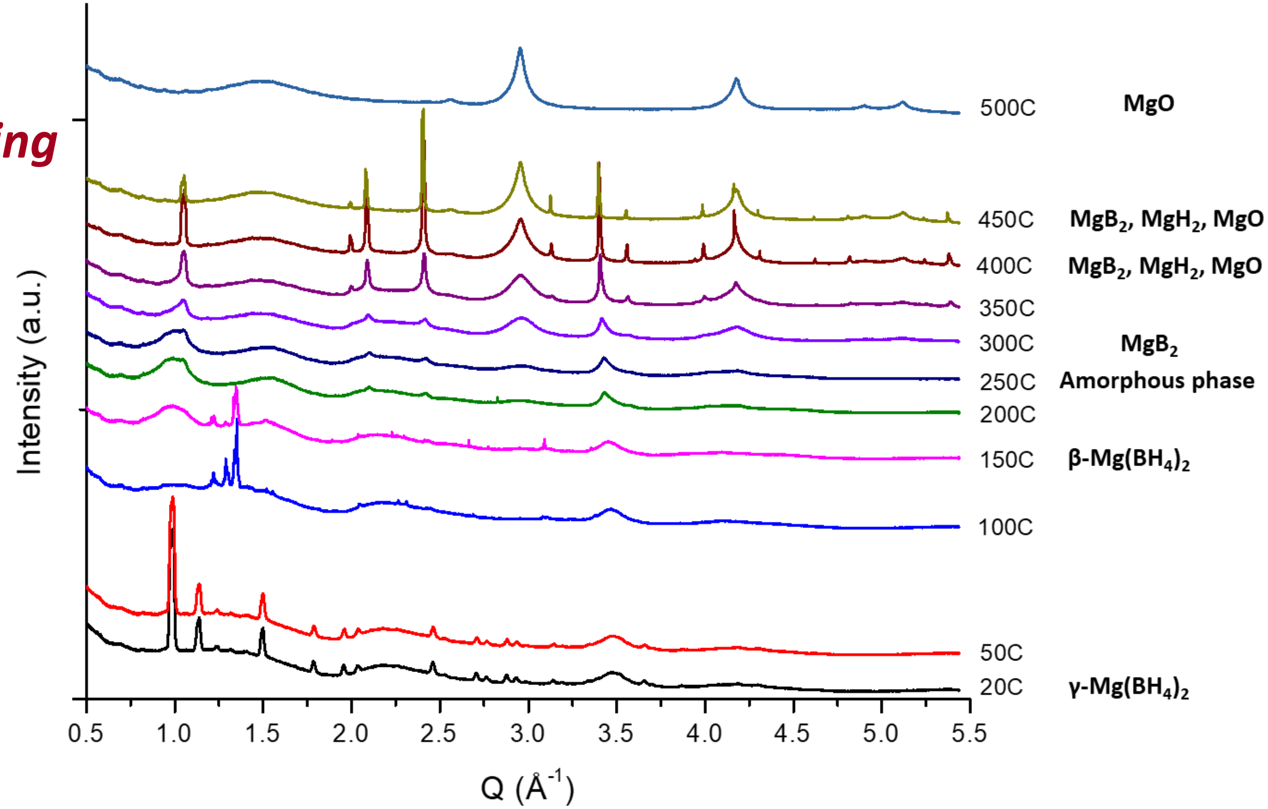
Early work focuses on polymorph evolution as a function of temperature and structure solution for new materials

SSRL BL 7-2; E = 14keV

γ-Mg(BH4)2 with TiN coating

- *Provided sample cell which improved on signal to noise and 2x increase of Q-range*
- *Established ability of sample cell to record structure over complete decomposition pathway*

NREL Transforming ENERGY



Two SSRL proposals submitted for chemical hydrides during 2018 issuing a combined time of 114 cycles (408 hrs beam time) over two year lifetime of proposal

Accomplishments : Total Scattering Analysis – Pair Distribution Function – APS BL 11-ID-B

SLAC

2.D Focus Area: Nanoscaling to improve thermodynamics and kinetics

New experimental approaches toward nanoscaling $Mg(BH_4)_2$

- Modifications to synthesis method
- Infiltration/growth within a porous framework

In conventional XRD, nanoscale effects appear as diffuse scattering or peak broadening

- Localized disorder does not propagate on a long-range scale and thus cannot easily be determined from XRD

How do we examine this disorder experimentally? → *Total Scattering Analysis*

Need: High resolution, good counting statistics, broad Q-range

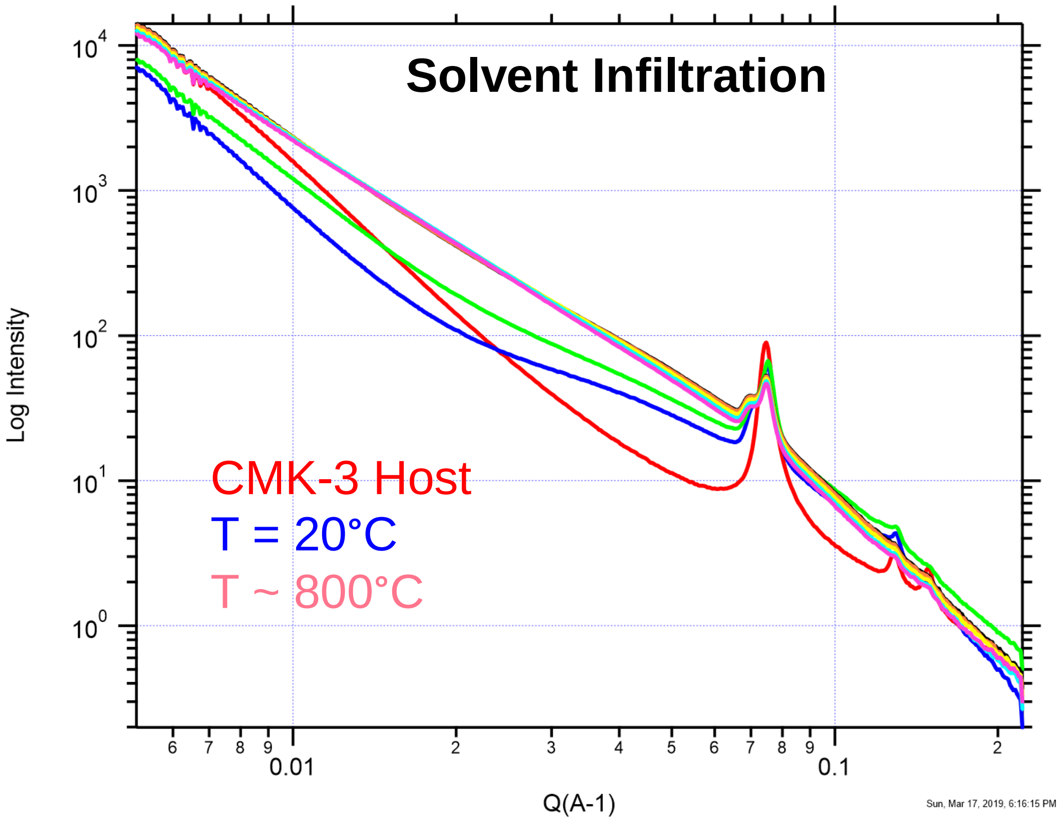
$$I(Q) \rightarrow S(Q) \rightarrow F(Q) \rightarrow G(r)$$

Average interatomic distances	→	PDF peak position
Structural disorder	→	PDF peak width
Averaged coordination properties	→	Integral intensity of PDF peaks
Particle size effect	→	PDF peak cut off

Proposal submitted for chemical hydrides during 2018 for APS 11-ID-B

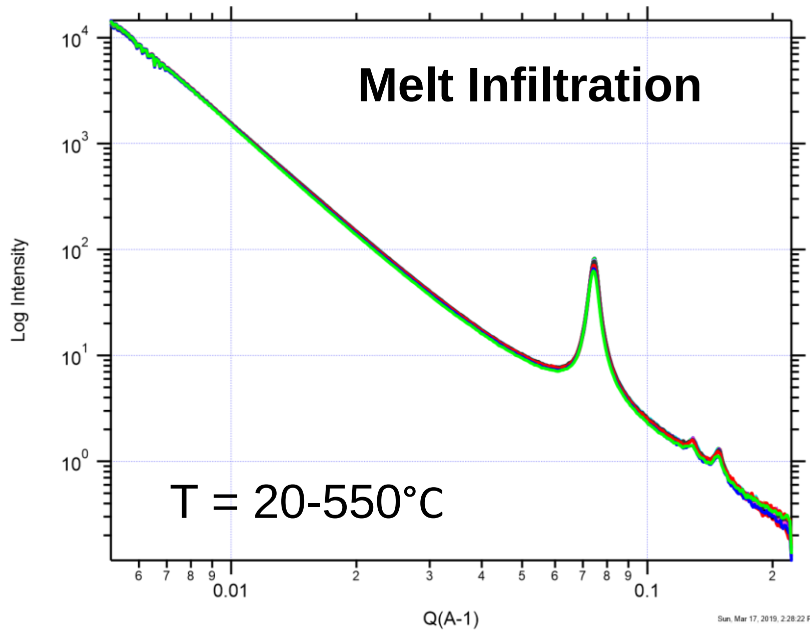
Accomplishments : *In Situ* Small Angle X-Ray Scattering (SAXS) – BLs 1-5, 4-2

SLAC



Sandia National Laboratories

CMK-3 templated carbon infiltrated with $Mg(BH_4)_2$



- Solvent infiltration method results in MBH infiltrated with a broad size distribution centered around d ~ 8 nm
- Melt infiltration has uniformly sized MBH domains

Two SSRL proposals submitted for chemical hydrides during 2018 issuing a combined time of 114 cycles (408 hrs beam time) over two year lifetime of proposal

Accomplishments- Seedling support: *Ex Situ* Small Angle X-Ray Scattering (SAXS/WAXS) – BLs 1-5, 4-2

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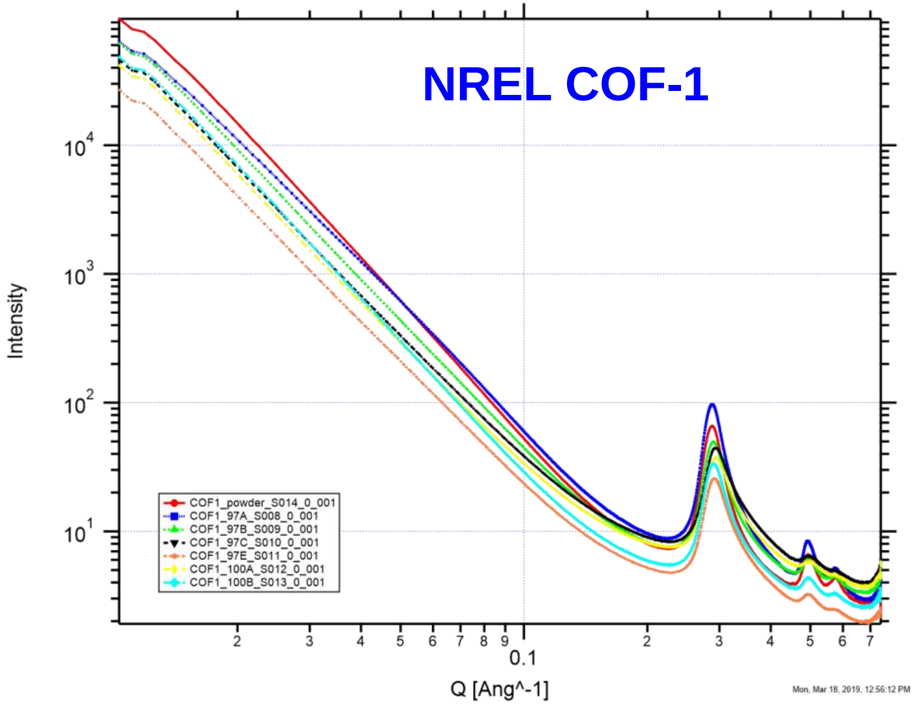
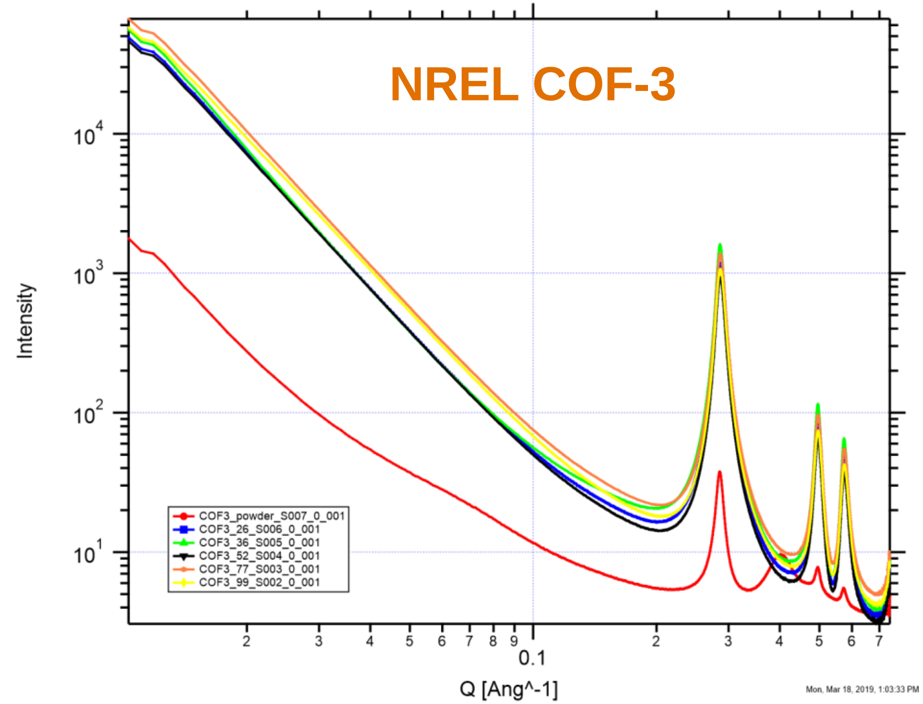
SSRL BL4-2; E = 11 keV; 1 sec exposure time





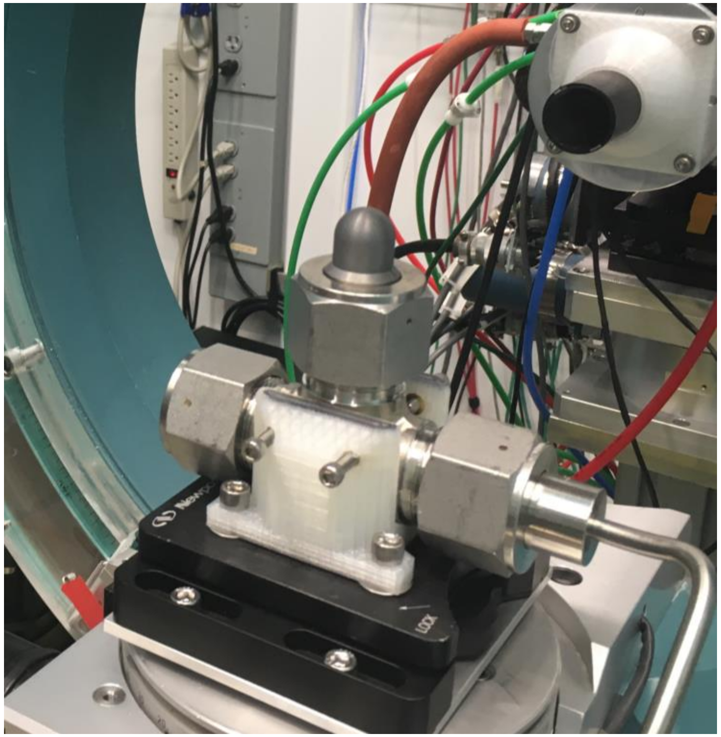
NREL Transforming ENERGY

- **COF-1** exhibits significant layer disorder and loss of scattering signal for the <110> and <200> reflections
- **COF-3** results in significantly greater stacking order with virtually no loss of intensity from <110> and <200> reflections

Two SSRL proposals submitted for chemical hydrides during 2018 issuing a combined time of 114 cycles (408 hrs beam time) over two year lifetime of proposal

Beryllium-Dome *In Situ* Sample Cell

In situ sample cell for X-Ray Absorption Spectroscopy (XAS), X-Ray Raman (XRR)



Interfaces with NREL gas handling manifold for variable pressure investigations

Used previously at SSRL
BL 4-1, 6-2b

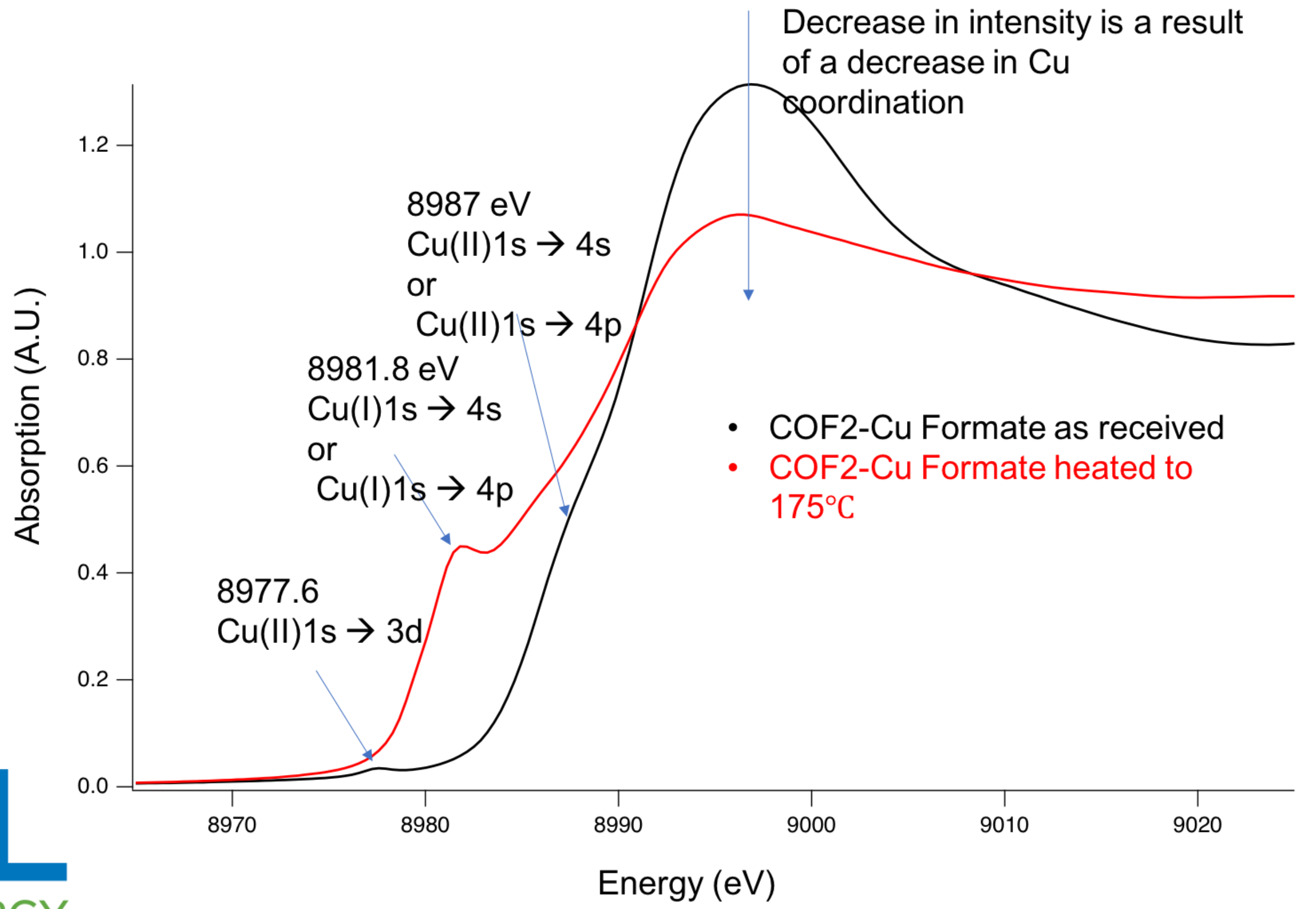
- Temperature limited to <400°C
- Maximum pressure of ~100 bar

Accomplishments: Seedling support
X-Ray Absorption Spectroscopy (XAS)

SLAC

SSRL BL 4-1

Cu(II)-formate bound to the COF framework was successfully converted to Cu(I) through heating at 175°C.



NREL Transforming ENERGY

Two SSRL proposals submitted for chemical hydrides during 2018 issuing a combined time of 114 cycles (408 hrs beam time) over two year lifetime of proposal

Proposed Future Work

Additional SSRL proposal submission for characterization of porous liquids task within carrier task 3

THF-coordinated $Mg(BH_4)_2$ structural characterization within the hydride task 2

Experimentally establish/optimize *in situ* high pressure re-hydrogenation capabilities for XRD, SAXS at SSRL. For multiple task and seedling work

Additional Opportunities at SLAC

- Resonant X-Ray Diffraction – lattice site/element specificity
- Reflectometry – depth profiling for films
- X-Ray Raman Scattering – allows enhanced in situ conditions compared to soft XAS
- LCLS Capabilities – dynamic materials, pump-probe experiments

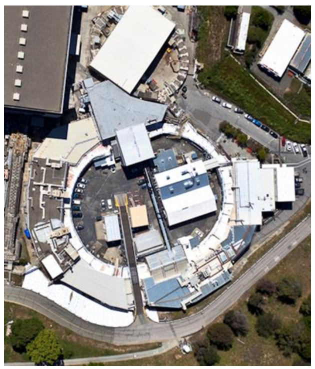
Summary

- Implemented new sample cell and demonstrated improved S/N over a broad Q and temperature range
- Generated 3 new beam time proposals (SSRL-2, APS-1) and received time for XRD, SAXS, XAS, and PDF for the HyMARC program over two years
- Demonstrated high-resolution decomposition and phase determination of $Mg(BH_4)_2$ via XRD
- Demonstrated the capabilities of *in situ and ex situ* SAXS/WAXS for MBH infiltrated in porous hosts and COF materials

Capabilities at SLAC: Stanford Synchrotron Radiation Lightsource
(Collaboration opportunities for seedling projects)

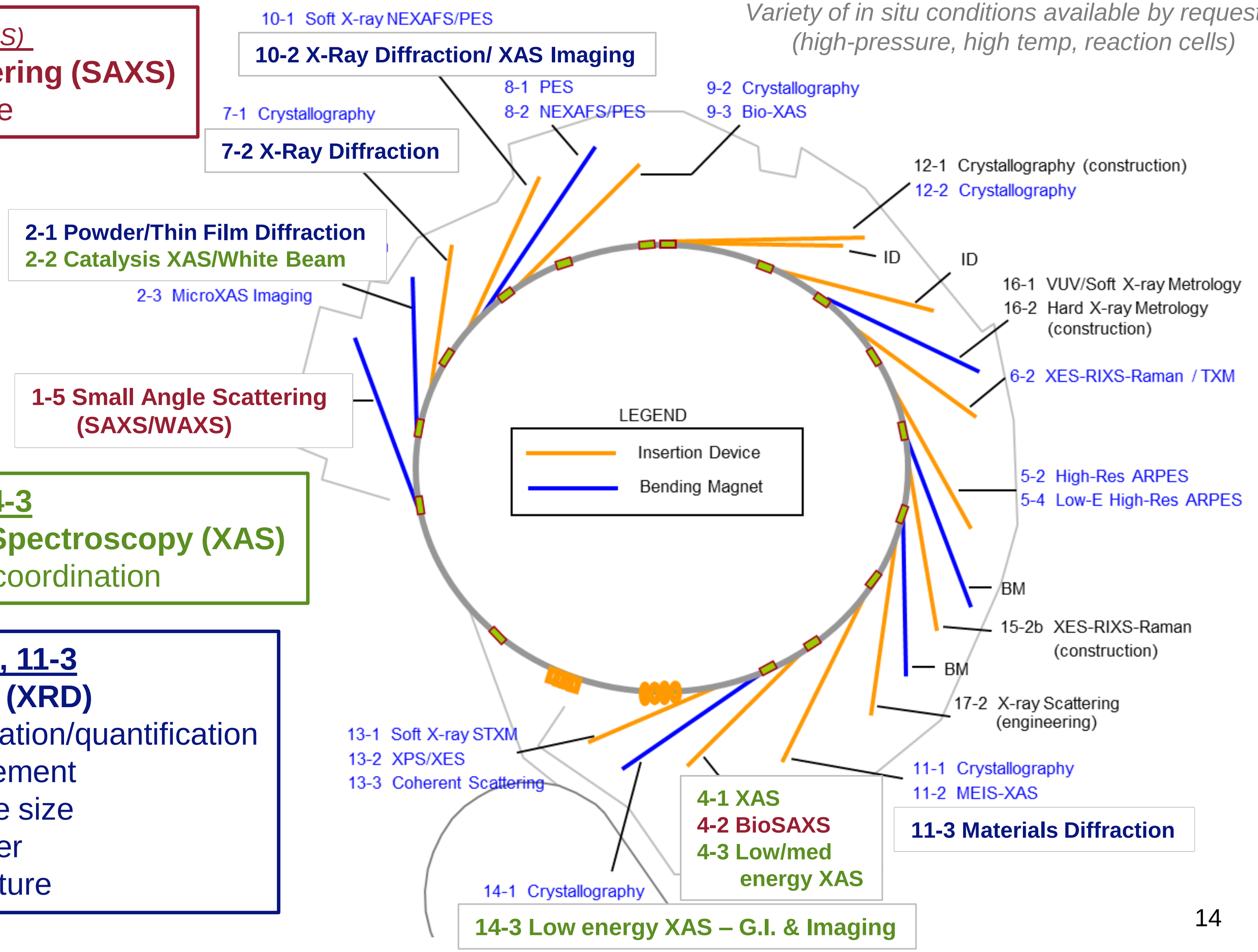
Variety of in situ conditions available by request (high-pressure, high temp, reaction cells)

BLs 1-5, 4-2 *(BioSAXS)*
Small Angle Scattering (SAXS)
- Pore/particle size



BLs 2-2, 4-1, 4-3, 14-3
X-Ray Absorption Spectroscopy (XAS)
- Oxidation state, coordination

BLs 2-1, 7-2, 10-2, 11-3
X-Ray Diffraction (XRD)
- Phase identification/quantification
- Atomic arrangement
- Grain/crystallite size
- Defects/disorder
- Orientation/texture



SSRL Materials Scattering Beamlines and Their Uses

Beamline	2-1	10-2 & 7-2	11-3	1-5
Detector	Point, Area	Point & Area	Area	Area
Advantages	• High resolution • Accurate peak position/shape • Weak peaks • Variable energy *(E = 5.5 – 17.5 keV)*	• High resolution • Accurate peak position/shape • Weak peaks • Variable energy *(10-2: 4.5 – 22 keV)* • 6/4 degrees of motion	• Fast measurement • Collect (nearly) whole pattern	• Fast measurement • Large features • Variable energy *(Usually @ 15.5 keV)* • Low background • Simultaneous WAXS available
Disadvantages	• Only 2 axes of motion	• Can be difficult to find textured peaks • Complicated • Fixed wavelength *(7-2 @ 14 keV)*	• Fixed wavelength *(E = 12.7 keV)*	• Small q-range • Background sensitive • Difficult interpretation
Methods	• Powders • Thin Films • Reflectivity • θ-2θ • Anomalous diffraction	• Single crystals • Grazing-incidence • Anomalous diffraction • Surface studies	• Thin films • Texture • Real time experiments • Polycrystalline/small grains	• Thin films • Real time experiments • Solution phase • Transmission

Increasing Our Scientific Impact Over the Next Decade

LABORATORY GOALS

Be the world leader in X-ray and ultrafast science and in our selected areas of accelerator science and high energy physics

Expand and increase our impact in Office of Science mission areas by leveraging our world-leading core capabilities and expertise

Broaden and strengthen our impact across critical national needs by using our position within Stanford and Silicon Valley

Be the “best-in-class” DOE lab for safe, efficient and innovative operations that align with and enable our research mission

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