HyMARC: A Consortium for Advancing Solid-State Hydrogen Storage Materials

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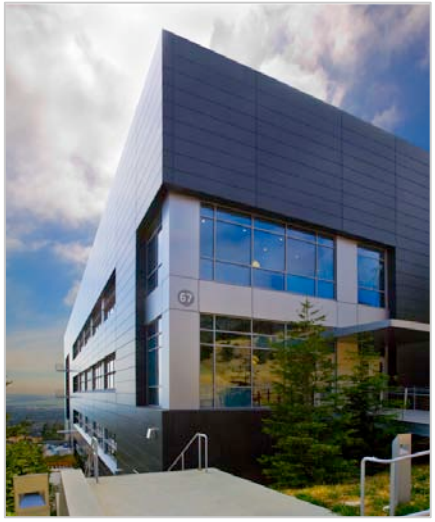
2016 DOE Hydrogen Annual Merit Review
June 8, 2016



Project ID: ST130

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview (LBNL)

Timeline

Project start date: 09/21/2015
Phase I end date: 09/30/2018

Barriers addressed

- Lack of understanding of hydrogen physisorption and chemisorption (Barrier O)
- System weight and volume (Barrier A)
- Charge/discharge rate (Barrier E)

Budget

FY15 DOE Funding: $250K
FY16 Planned DOE Funding: $590K
Total Funds Received: $840K

Team

Funded Partners:
Sandia National Laboratories (lead)
Lawrence Livermore National Laboratory

Relevance and Objectives

HyMARC will provide **community tools** and **foundational understanding** of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials

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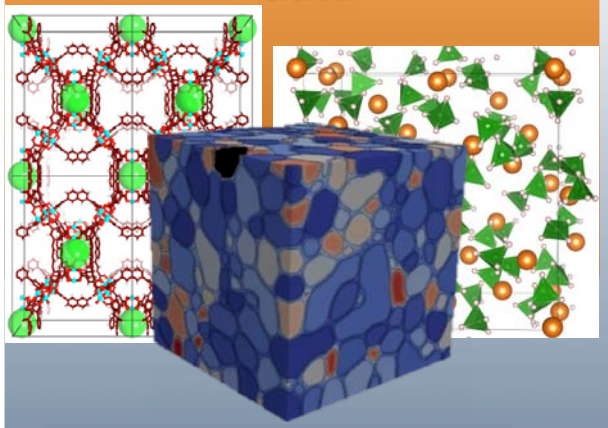
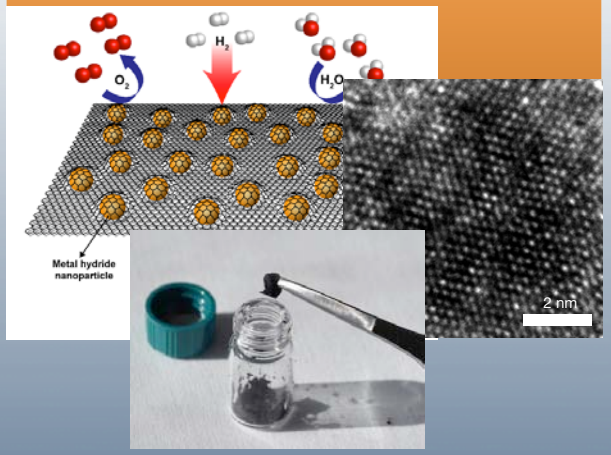
Theory, simulation, & data



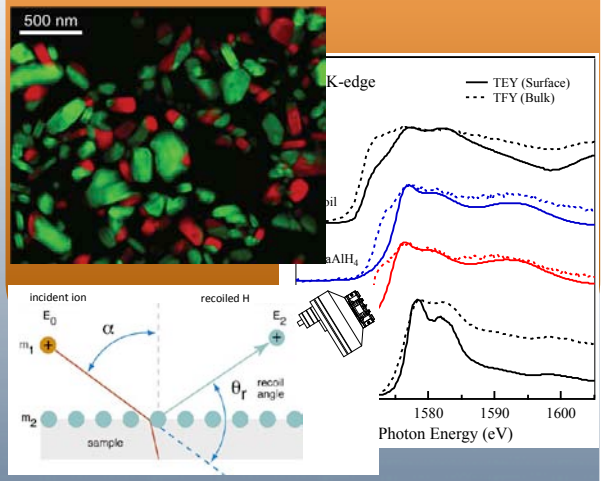
- Quantum Monte Carlo for sorbents
- **DFT and *ab initio* molecular dynamics for bulk/surface/interface chemistry**
- Classical MD & kinetic Monte Carlo for non-equilibrium transport
- Phase-field modeling for solid-state phase transformation kinetics
- **Computational spectroscopy**
- **Community software & databases**

Controlled synthesis



- Metal organic frameworks (MOFs)
- Hierarchical integrated bulk and nanoscale metal hydrides
- High-pressure synthesis
- **Functionalized carbon encapsulants and porous nanoconfining media**
- Sorbent suite for model testing and validation

In situ characterization



- **Ambient-pressure XPS**
- **Soft X-ray absorption and emission spectroscopy**
- **Electron microscopy and X-ray spectromicroscopy**
- Low-energy ion scattering for surface hydrogen detection

Relevance (LBNL-specific): Materials by Design coupled with Advanced Characterization and Modeling

Project Objectives, overall:

- Focus on **light materials** and synthesis strategies with fine **control of nanoscale dimensions** to meet weight and volume requirements via encapsulation, confinement (A)
- Design **interfaces with chemical specificity** for thermodynamic and kinetic control (E) of hydrogen storage/sorption and selective transport
- Explore **novel storage concepts** and/or obtain **fundamental understanding** of "established" processes via known/idealized systems/materials (O)
- Develop in situ/operando **soft X-ray characterization** capabilities in combination with **first-principles simulations** to extract atomic/molecular details of functional materials and interfaces (O)
- Refine chemical synthesis strategies based on atomic/molecular scale insight from characterization/theory

Establish expertise and capabilities for the hydrogen storage community

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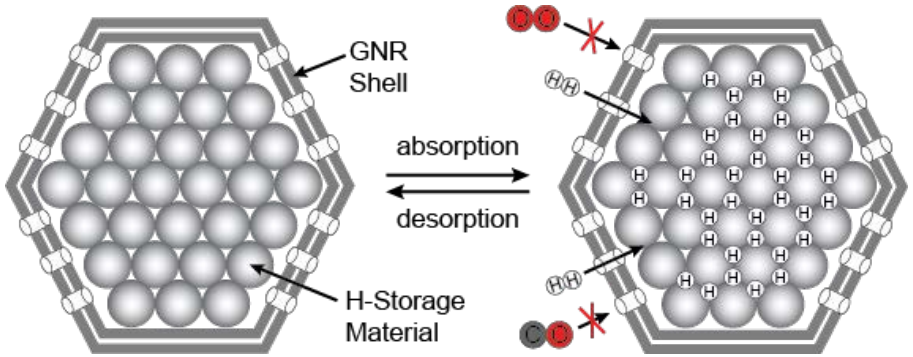
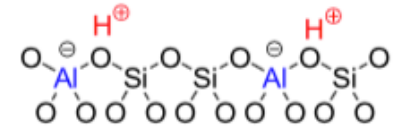
Relevance: Encapsulated metal hydrides, Lewis acid-base sorbents, MOF isotherms

FY16 Project Objectives:

- Establish rGO/Mg as new system to understand transport at heterogeneous solid/solid interface
- Synthesize & characterize hybrid Mg-NP and functionalized GNRs – platform for new type of additive using GNR chemistry
- Understand and measure hydrogenation kinetics: assess performance of GNR as additive

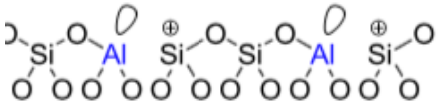


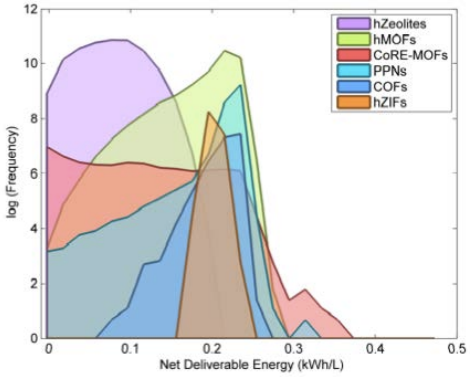
- Synthesize mesoporous and microporous silica with Al grafting to enhance H_2 absorption
- Measure high-P H_2 absorption
- Characterize Al coordination using X-ray spectroscopy/theory



Brønsted acid sites

Lewis acid sites (e^-)





- Computational exploration of MOF adsorption isotherms within CORE Database

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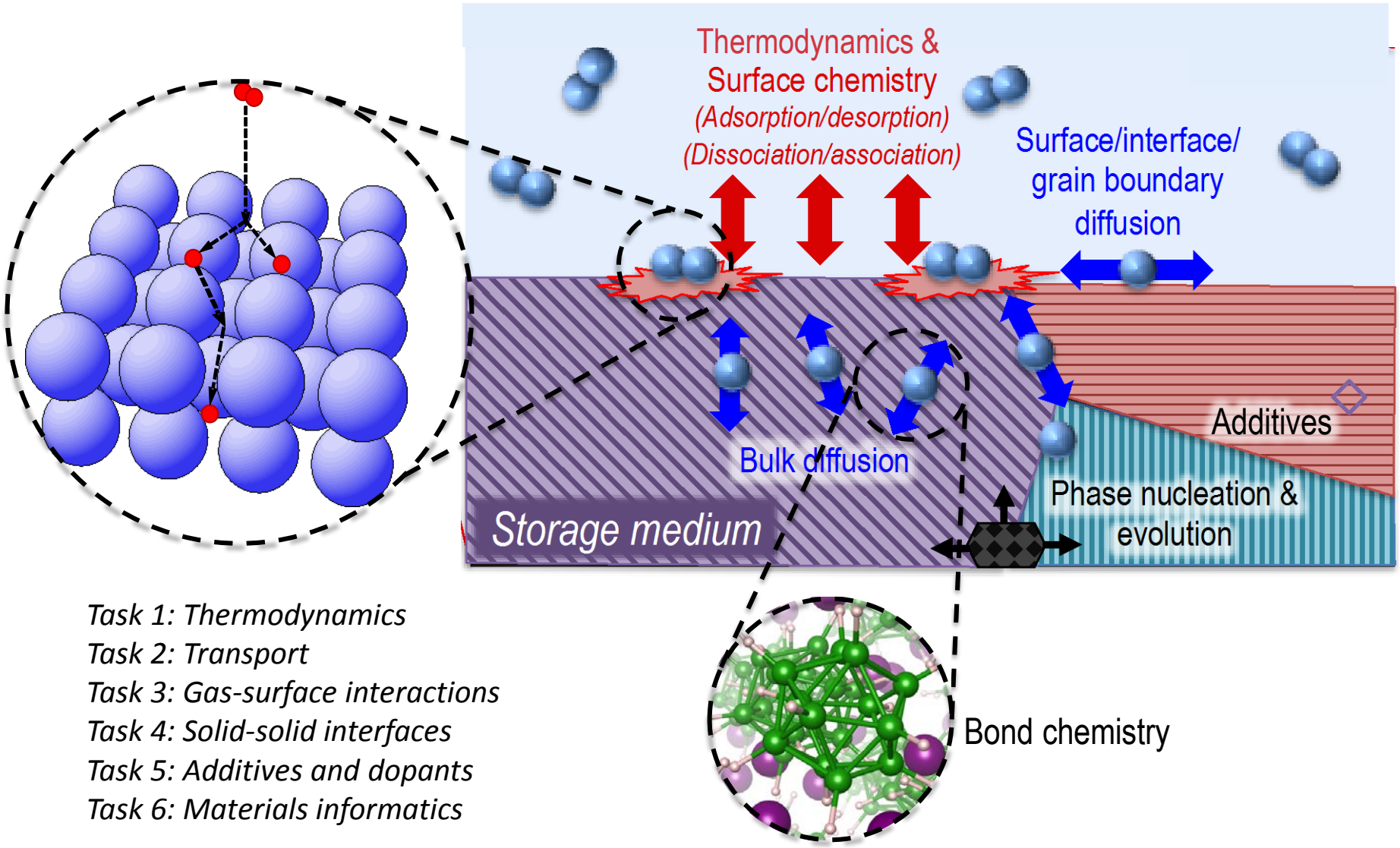
Approach: HyMARC Tasks Target Thermodynamics and Kinetics



Task 1: Thermodynamics
Task 2: Transport
Task 3: Gas-surface interactions
Task 4: Solid-solid interfaces
Task 5: Additives and dopants
Task 6: Materials informatics

Technical Approach: Contributions of LBNL to HyMARC, Integration Across All Tasks, Access to All Labs

Tasks	LBNL Team:
2,3,4,5	**Jinghua Guo** (jguo@lbl.gov): X-ray synchrotron spectroscopy (Tasks 2-5)
2,3,4,5	**David Prendergast** (DGPrendergast@lbl.gov): Computational spectroscopy (Tasks 2-5)
1,4	**Jeff Urban** (jjurban@lbl.gov): Phase transitions and nanoscale effects in hydrides
1,5	**Gabor Somorjai** (gasomorjai@lbl.gov): Functional sorbents
1	**Felix Fischer** (ffischer@lbl.gov): Functionalized graphene nanoribbons
6	**Maciek Haranczyk** (mharanczyk@lbl.gov): Materials genome for porous materials

Entire HyMARC Team accessing LBNL BES User Facilities

The Molecular Foundry (TMF):

- synthesis, characterization, and simulation of nanoscale materials/interfaces
- National Center for Electron Microscopy
- access to supercomputing (NERSC) through existing Foundry allocations

Advanced Light Source (ALS):

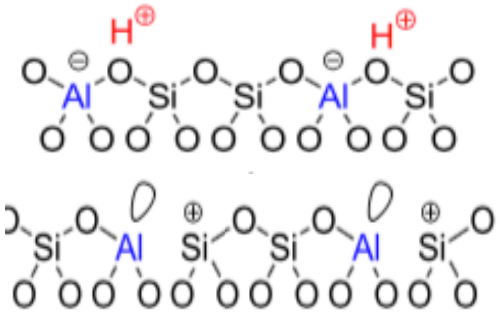
- Soft X-ray absorption/emission spectroscopies (XAS/XES) – in situ
- Ambient Pressure XPS
- Scanning Transmission X-ray Microscopy (STXM) and Ptychography

Active user projects at TMF and ALS and Approved Program Proposal @ ALS

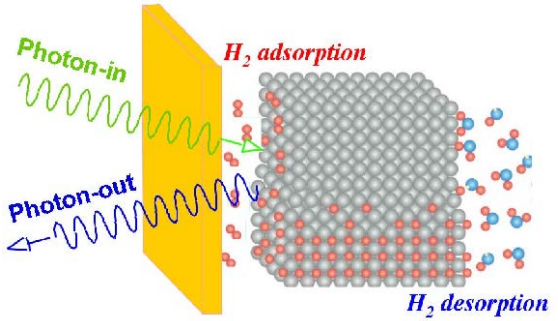
- partnership to foster a new soft X-ray H_2 storage user community

Technical Approach: Matched Novel Synthesis, Characterization, and Modeling for Storage Materials

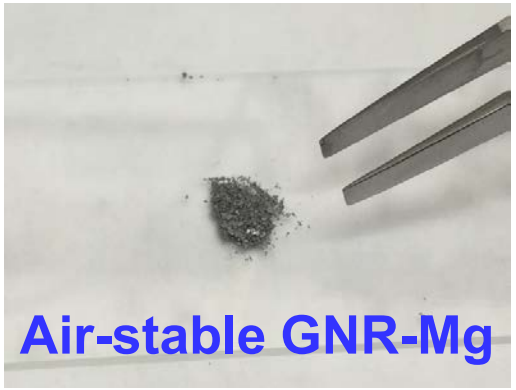
Theory & Design of Storage Materials



Characterization



Synthesis & Performance Evaluation



- Enabling approach: secure **user projects to Molecular Foundry and ALS**
- Innovative synthetic routes to metal hydrides and hybrid nanoscale systems that will reveal key phenomena governing H_2 release/absorption and motivate new H_2 storage materials
- Developing new acid/base concepts to modify the enthalpy of H_2 binding in sorbents
- Creating algorithms to enable computation of H_2 isotherms in framework materials
- *In-situ* spectroscopic and structural characterization techniques that establish the role of interfaces in controlling H_2-storage reaction mechanisms and pathways;
- X-ray spectroscopy interpretation models that allow structural, chemical and dynamic study of interfaces and additives in H_2 storage reactions.

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Planned Milestones and Status: FY16 and FY17

Q1: (S) Synthesize library of bulk-phase model storage systems for T1-T5
T1: Synthesize and characterize stable metal hydrides to match computation efforts (100%)
T1: Synthesize and characterize graphene nanobelts with targeted moities (100%)
T1: Synthesize and characterize new classes of mesoporous zeolites using acid-base concept (100%)
T1: Study GCMC simulations of absorption isotherms in open framework materials(100%)

Q2: (S) Demonstrate size control method for one prototype complex hydride nanostructure
T1: Perform reaction kinetics studies to determine design rules for nanoconfined metal hydrides (50%)

Q3: (C) Demonstrate in-situ soft X-ray AP-XPS, XAS, XES tools, with sample heating
T3, T5: Performed XAS spectroscopy of hydrides and dopants at LBL/ALS (50%)
T2: Perform first principles simulated X-ray spectroscopy to interpret synchrotron data (50%)
T3, T5: Indicate feasibility of STXM to study interface dynamics (50%).

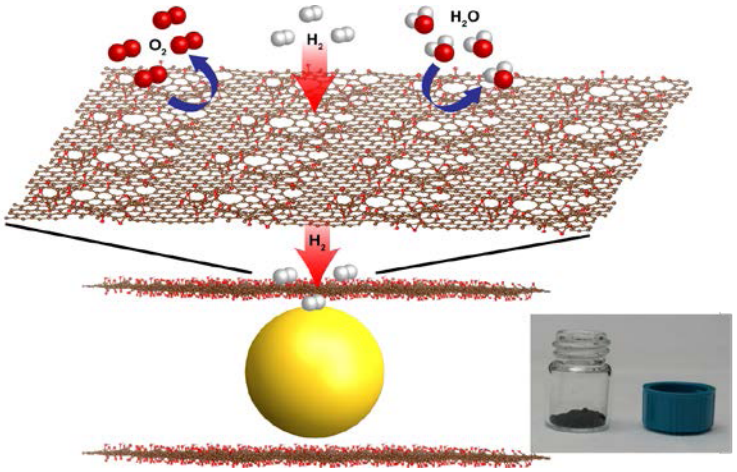
Q4: (C+T) Identify hydride mobile species and diffusion pathways
T5: Begin development of KMC framework for interface/amorphous transport (100%)
T5: Assessment of acid-catalyzed moities for modifying sorbent enthalpies (50%)
T5: STM studies of catalytic sites before/after H_2 exposure (20%)
T5: synthesize catalytically functionalized GNRs (70%)

Q4: (S+C) Synthesize library of nanoparticles: 1 – 5 nm, 5 – 10 nm, > 10 nm for one prototype hydride
T1-T5: Select model materials for facilitating experiment-theory feedback within each task (50%)

Task 1 Accomplishment: Multilaminates of Mg Nanocrystals and Reduced Graphene Oxide (rGO-Mg)

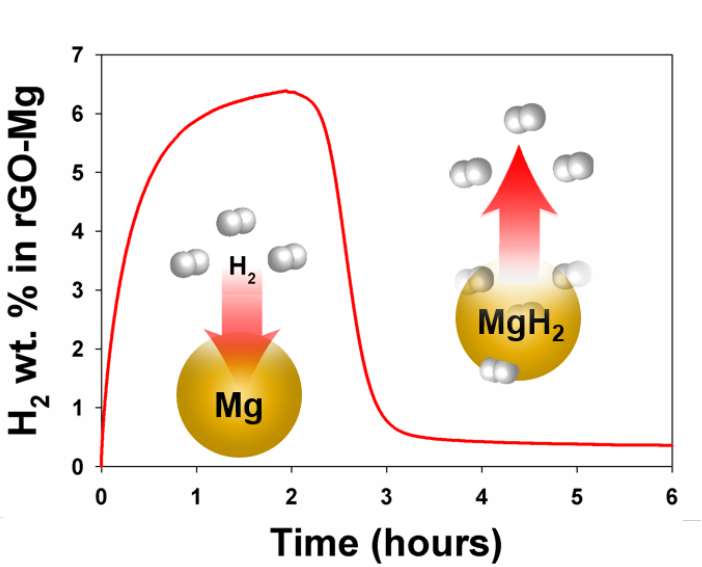
Achievement: Light-weight (few layers GO) air-stable high-performance (~7wt% full composite) rGO-Mg

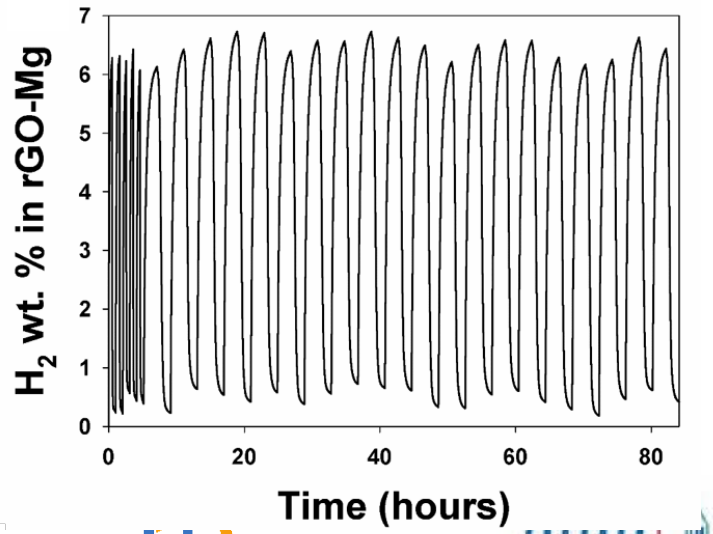
T1 Milestone: Very stable well-controlled hydride system for matching computational studies



rGO layers encapsulating Mg crystals function as both hydrogen selective protecting matrix and catalysis.

Collaboration with Jinghua Guo & Yi-Sheng Liu (ALS, LBNL)





(1) E. Cho, A. M. Ruminski, S. Aloni, Y-S. Liu, J. Guo, J. J. Urban, *Nature Communications* (2016).

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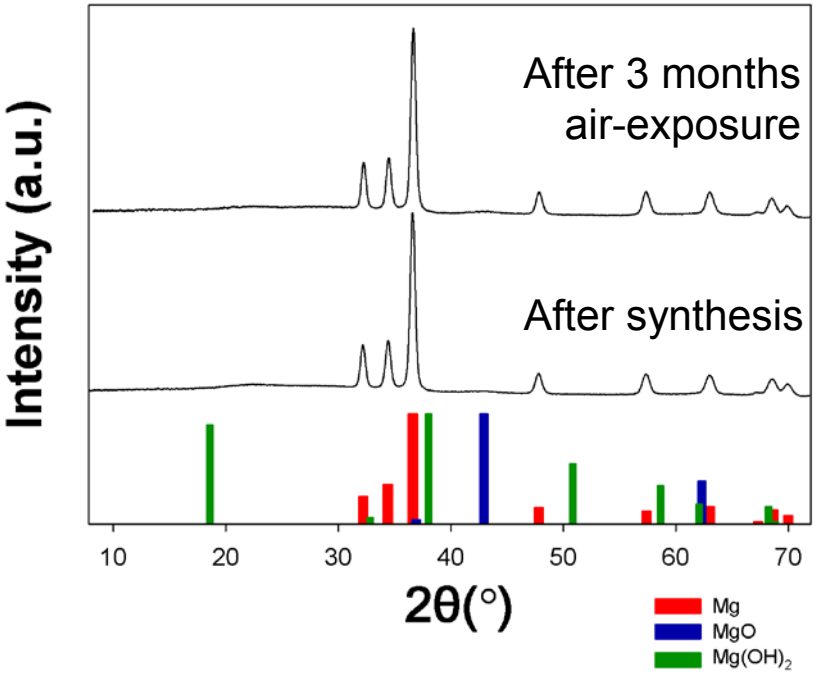
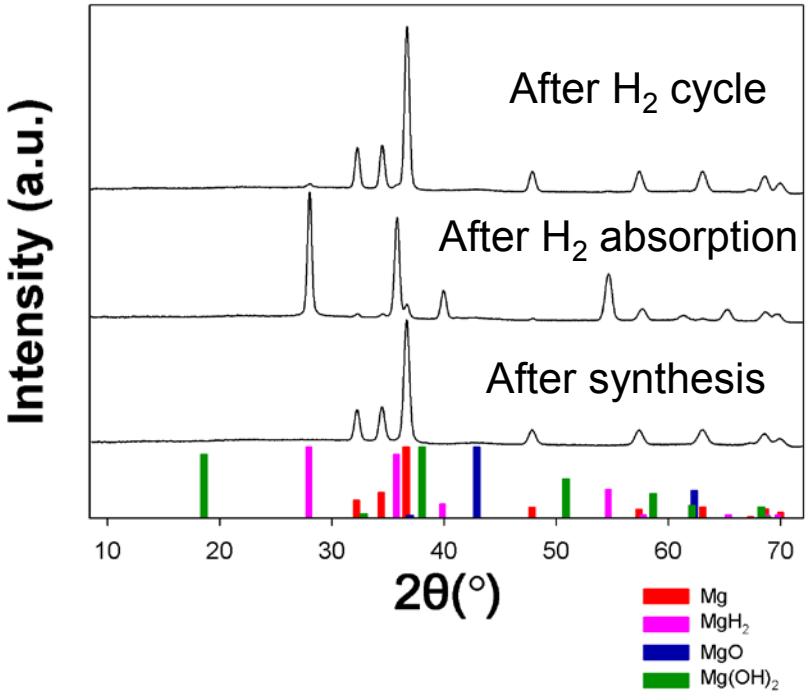
Task 1, 3 Accomplishment: Synthesized Mg-GNR Composite Material

- T1 milestone: A flexible GNR-based matrix has been developed that stabilized high surface area reactive Mg nanoparticles without preventing H_2 transport processes.

Stabilization of highly reactive metal NPs by GNR matrix

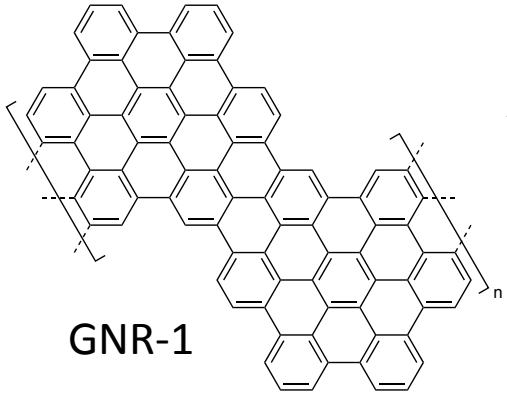


Exhaustive and reversible H_2 absorption/ desorption

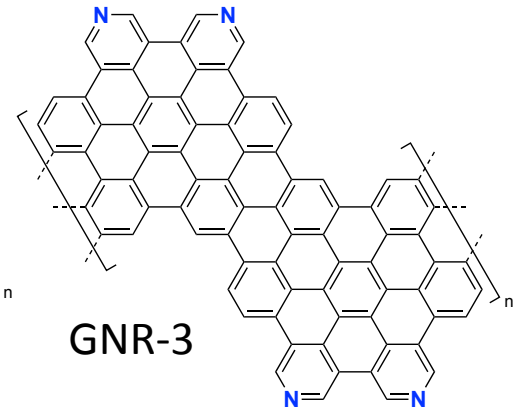


Task 1, 5 Accomplishment: Absorption/Desorption Kinetics Correlate with Functionalization of GNRs

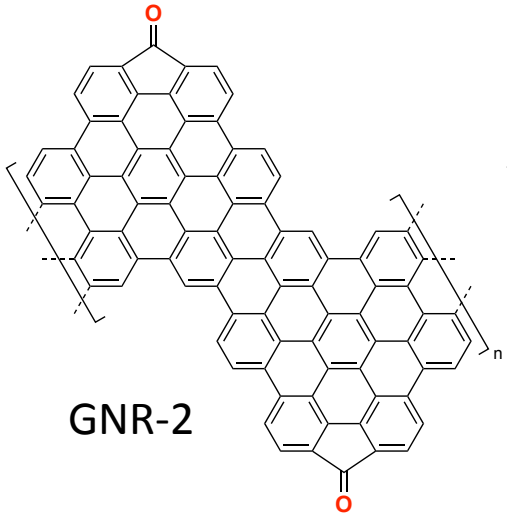
- T1,5 accomplishment: Chemical functionalization of the GNR matrix has a direct influence on the absorption and desorption kinetics. Potential synthetic handle to tune the performance of H_2 storage material.



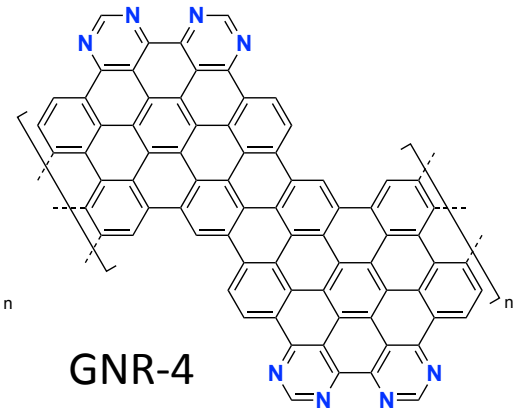
GNR-1



GNR-3



GNR-2



GNR-4

Maximum Capacity

wt.% H_2	Absorption	Desorption
GNR-1	7.1 %	-6.7 %
GNR-2	7.3 %	-7.0 %
GNR-3	7.2 %	-6.9 %
GNR-4	7.3 %	-6.8 %

Activation Free Enthalpy

	Absorption	Desorption
GNR-1	91.8 kJ/mol	160.0 kJ/mol
GNR-2	85.3 kJ/mol	172.2 kJ/mol
GNR-3	91.5 kJ/mol	130.4 kJ/mol
GNR-4	90.4 kJ/mol	156.0 kJ/mol

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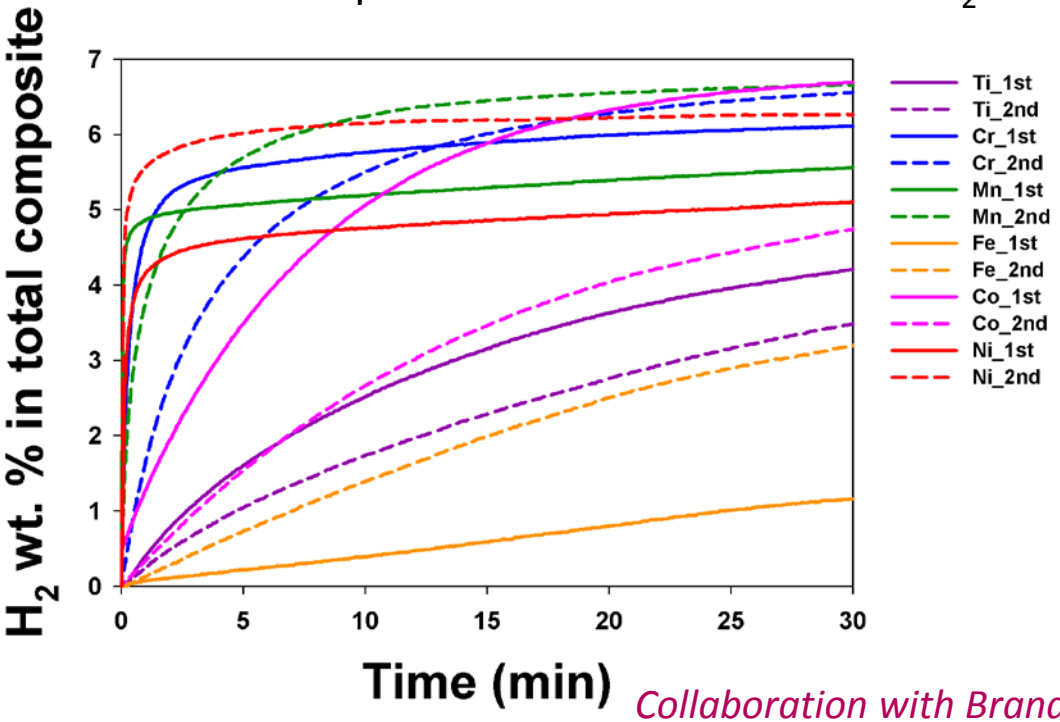
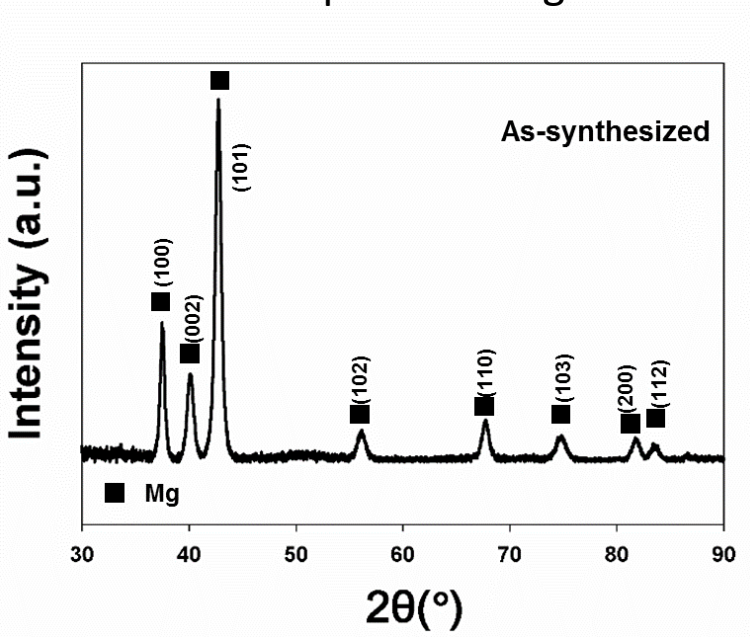
Task 5 Accomplishment: 3d-Transition Metal (TM) Doped rGO-Mg

Milestone: 5 mol.% TM dopants enhance H_2 sorption kinetics without sacrificing the high H_2 capacity of rGO-Mg

Hydrogen absorption of rGO-Mg with different TM dopants at 200 °C and 15 bar of H_2



Representative crystal structure of TM doped rGO-Mg



Collaboration with Brandon Wood (LLNL) and Xiaowang Zhou (Sandia)

Different kinetics depending on the dopants and the 1st & 2nd absorption behave in a different way!

(1) E. Cho, A. M. Ruminski, Y-S. Liu, J. Guo, J.J. Urban, *in preparation*.

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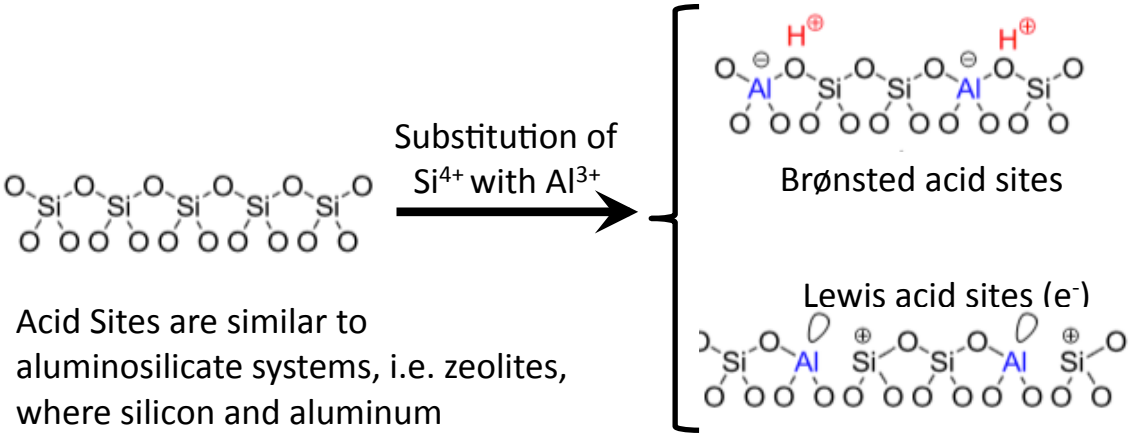
Task 5 Accomplishment: Meso- and Micro-porous silica with Al grafting for acid catalyzed sorption

Aluminum grafting of meoporous silica support



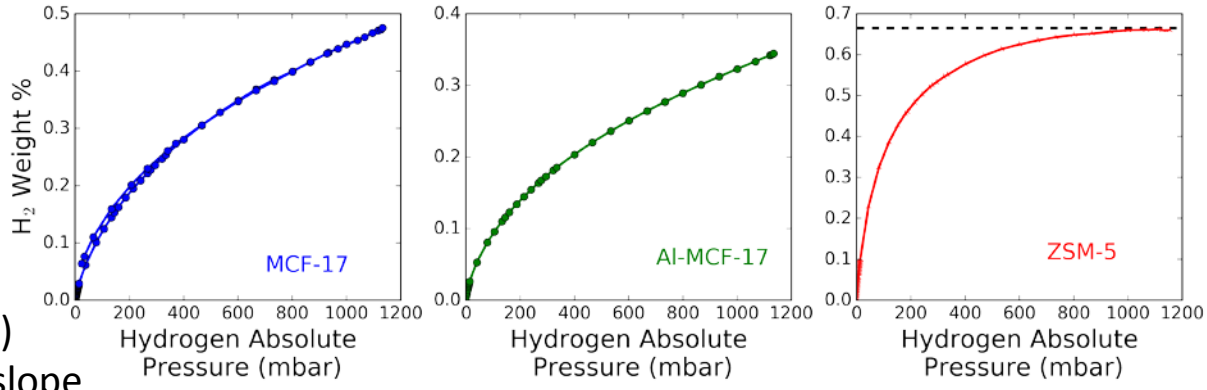
Acid Sites are similar to aluminosilicate systems, i.e. zeolites, where silicon and aluminum precursors are mixed together

Physisorption of N_2 at LN_2 temp

	BET (m^2/g)	Average Pores	Si:Al ratio*
MCF-17	672.6	23.6	0
Al-MCF-17	473.2	25.0	9
ZSM-5	462.8	19.2	33

MCF-17 = Mesoporous silica
Al-MCF-17 = Al-grafted MCF-17
ZSM-5 = Mesoporous zeolite

H_2 adsorption @ LN2 temp
0.1 - 1200 mbar



ZSM-5: "plateau"
P > 800 mbar (max =~0.66%)
MCF-17 and Al-MCF-17: positive slope
storage capacity may increase with **high P (to be measured at Sandia)**

Gabor Samorjai and Gerome Melaet

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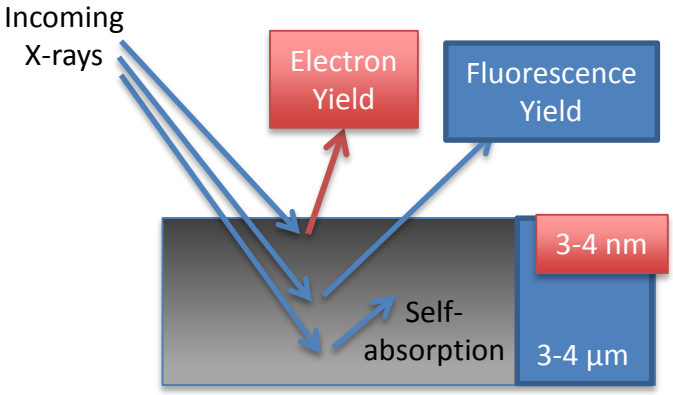
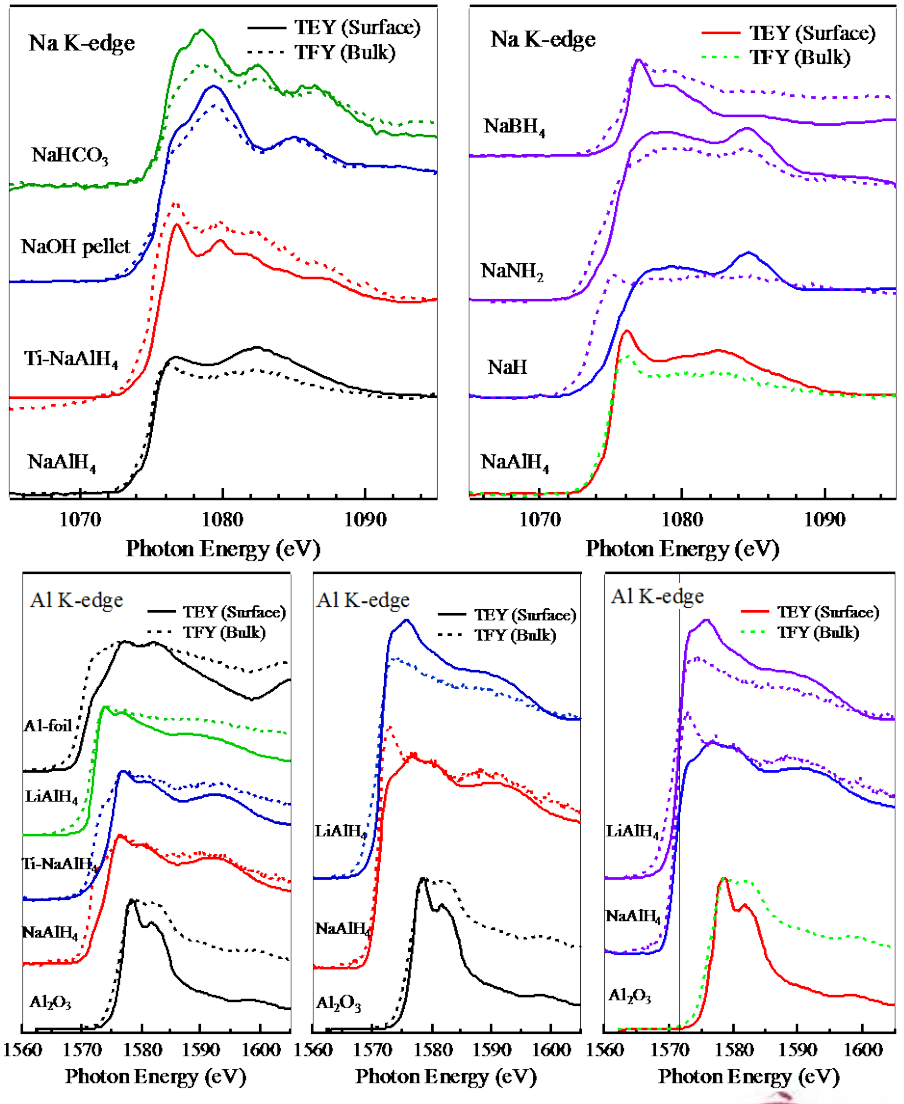
Task 3,4,5 Accomplishment: Established soft X-ray spectral signatures for Na and Al compounds

Soft X-ray (Na and Al K-edge) X-ray absorption spectra measured for various "standards" or model systems as references for future in-situ XANES of working materials

Bulk (TFY) and surface (TEY) sensitive measurements possible. TFY requires corrections for self-absorption
– maybe not an issue for porous frameworks or encapsulated nanoparticles





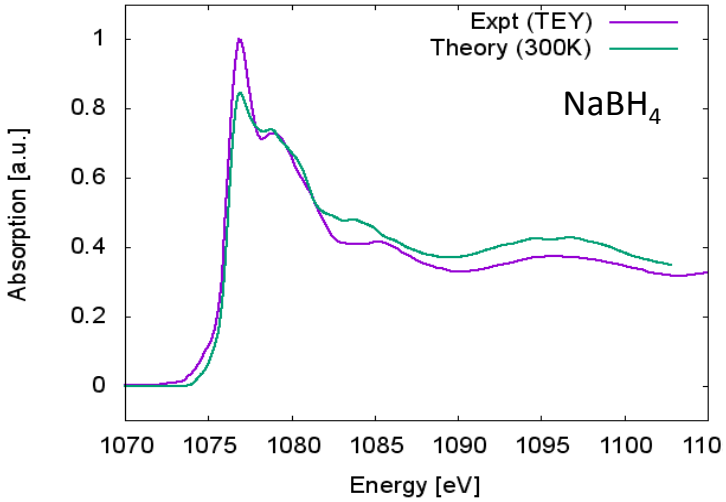
Samples: Vitalie Stavila and Mark Allendorf
XAS measurements: Jinghua Guo and Yi-Sheng Liu
Simulations: David Prendergast, Craig Schwartz, Jan Aeschlimann

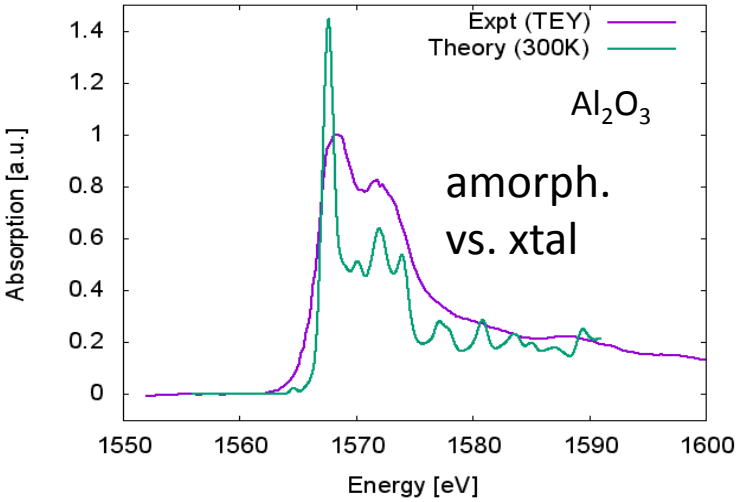
Accomplishment: Predictive first-principles method for interpretation of Na and Al K-edge XANES

Peak positions qualitatively reproduced

Line-shape agreement

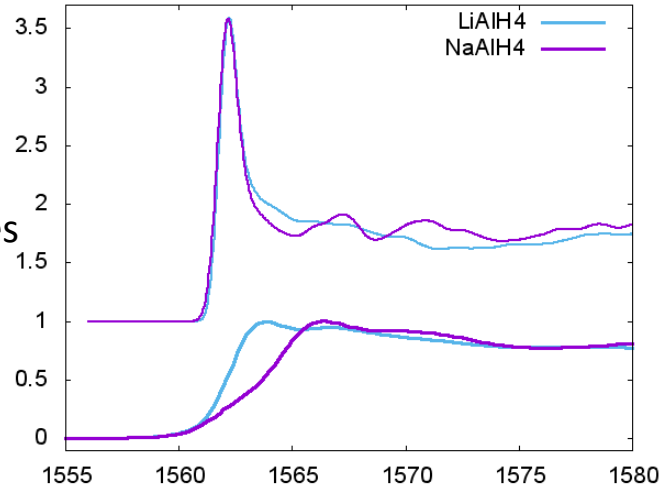
finite T produces pre-edge features

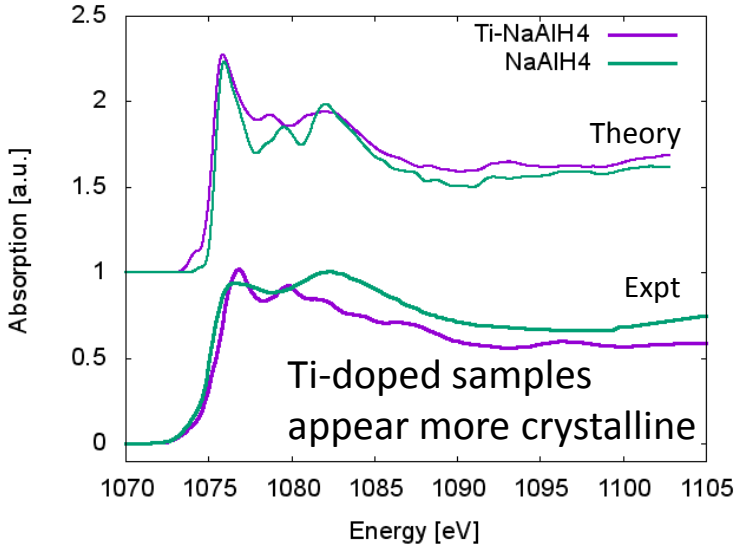




Theoretically Al K-edge of Li and Na alanates almost identical (AlH_4^-)

But experiment indicates presence of different local Al chemistry





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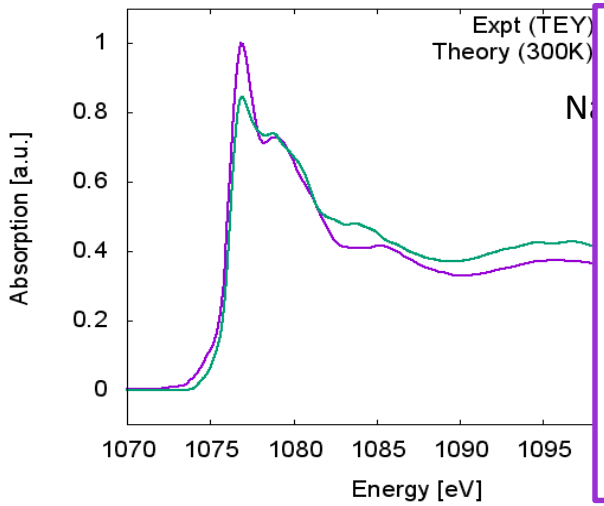
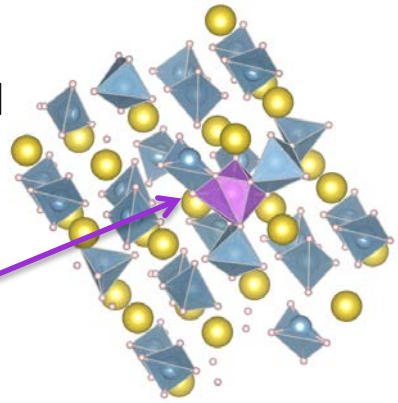


MD sims @ T=300K
Ti substituting for Al collects additional H atoms

$Ti\text{-}H_4$ ➔ $Ti\text{-}H_8$



H-atoms shared with nearby Al

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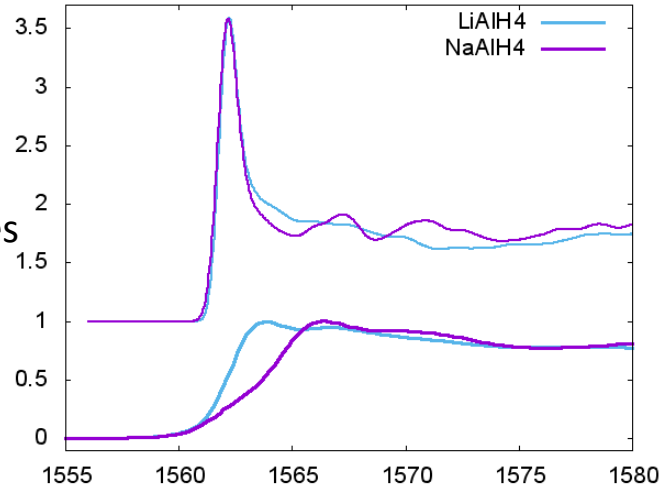
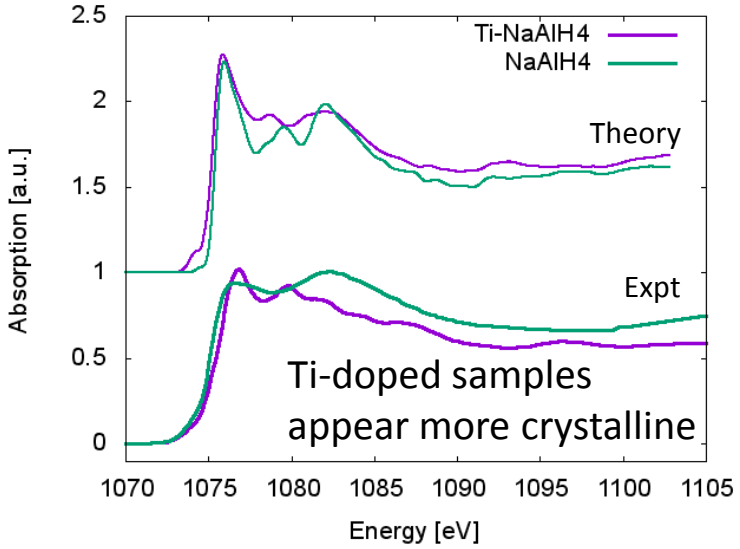
But experiment indicates presence of different local Al chemistry





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Simulations: David Prendergast, Craig Schwartz, Jan Aeschlimann

Collaborations external to HyMARC

- Aaron Thornton (CSIRO Australia) and Berend Smit (UC Berkeley/EPFL)
- "High-throughput computational screening of MOFs”
- University of Cape Town (South Africa). In situ time resolved XRD of GNR-Mg composites during absorption/desorption at process relevant pressures and temperatures.
- Extensive collaborations within and across HyMARC

Remaining Challenges and Barriers

- Synthesis of complex hydride nanoparticles and integration with graphene nanobelts
- Understanding the local chemistry of TM-dopants in alanates and hydrogen coordination with XANES validation
- Kinetics: Desorption in Hydrides
- High-P H_2 sorption profiles of Al-grafted porous silica to be measured in collaboration with SNL
- First-principles interpretation of STXM data and in situ XANES

Proposed future work

Milestone	Description	Task	Proposed completion
1	Continue to work on library of 1-5, 5-10, and >10nm hydride particles	1	Q4 FY16 (67% done)
2	Nanoscaled Metal Borohydride (e.g. $Mg(BH_4)_2$) for High-Capacity Hydrogen Storage	1	Q4 FY16 (10% done)
3	Initiate plasmonic studies of phase transformation in complex hydrides	4	Q2 FY17 (5% done)
4	First-principles molecular dynamics studies of Ti in LiALH4-thermodynamics and kinetics	5	Q4 FY16 (5% done)
5	Interpretation of encapsulated metal hydride spectroscopy and understanding of interfacial electronics	4	Q4 FY16 (5% done)
6	Lewis acid-Bronsted Base concepts demonstrated in real substituted silica templates	5	Q2 FY16 (50% done)
7	Advance capabilities of in-situ XAS and XANES to enable phase detection	3,4	Q2 FY17 (30% done)

Summary

- Berkeley Labs: Funded at start of FY16, Unique suite of synthetic hydride/graphene nanobelt, sorbent, in-situ X-ray, and modeling tools supporting HyMARC objectives

- FY16 LBNL modeling tasks focused on X-ray interpretation of ALS in-situ spectroscopy data
- FY16 LBNL synthesis tasks focused on establishing key **strategies for integrating metal hydrides with designer graphene nanoribbons**
- FY16 LBNL characterization tasks focused on X-ray detection of **spectroscopic changes upon hydrogenation** (complements LLNL activities)
- Funded beginning FY16, already delivering new materials, publications, IP
- We are moving toward complex hydrides and advanced instrumentation and modeling in FY17

Thank you for your attention!

Sandia National Laboratories

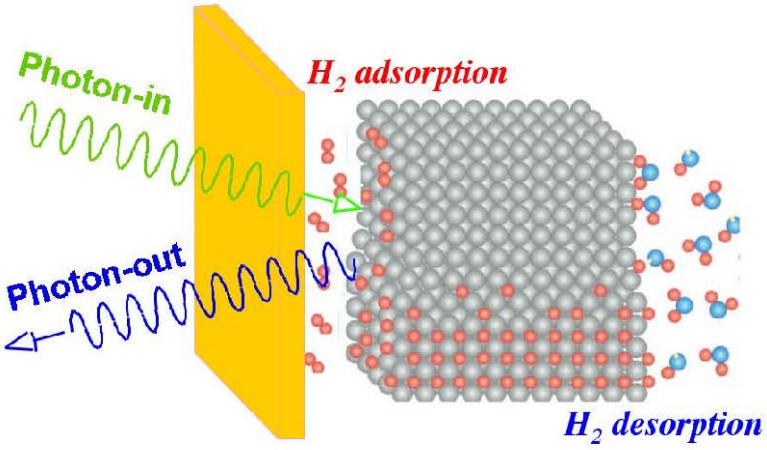
Lawrence Livermore National Laboratory

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

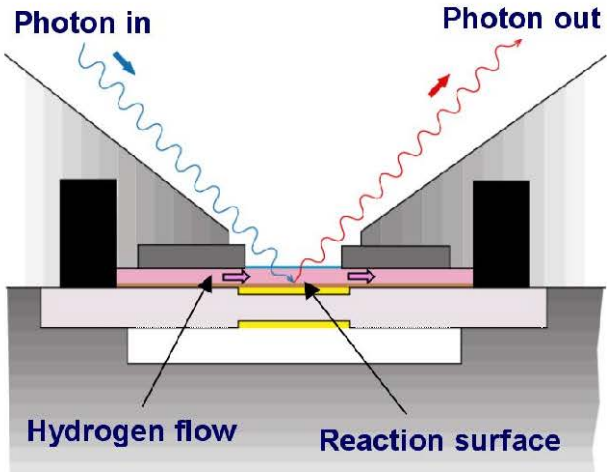
Technical Back-Up Slides

ALS: X-ray In-situ Characterization of Metal Hydrides

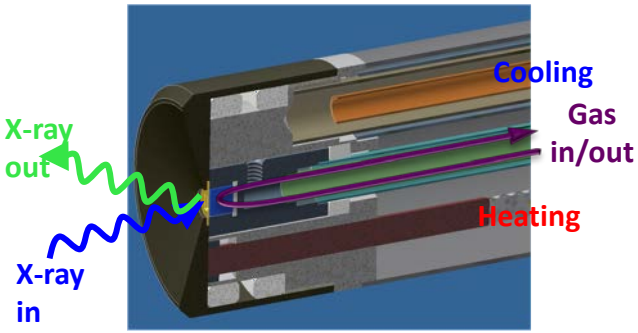
(A) Photon-in/photon-out soft-x-ray spectroscopic study



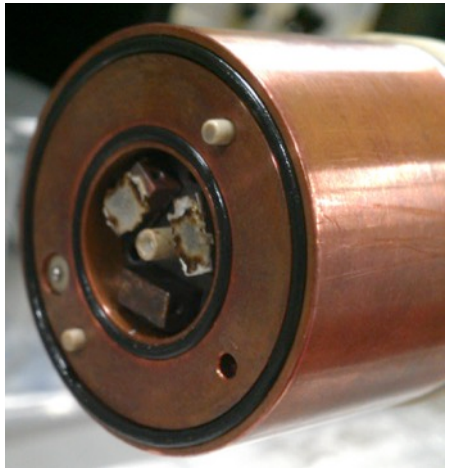
(B) A conceptual design of Hydrogen cell for in-situ study



Gas Flow Cell

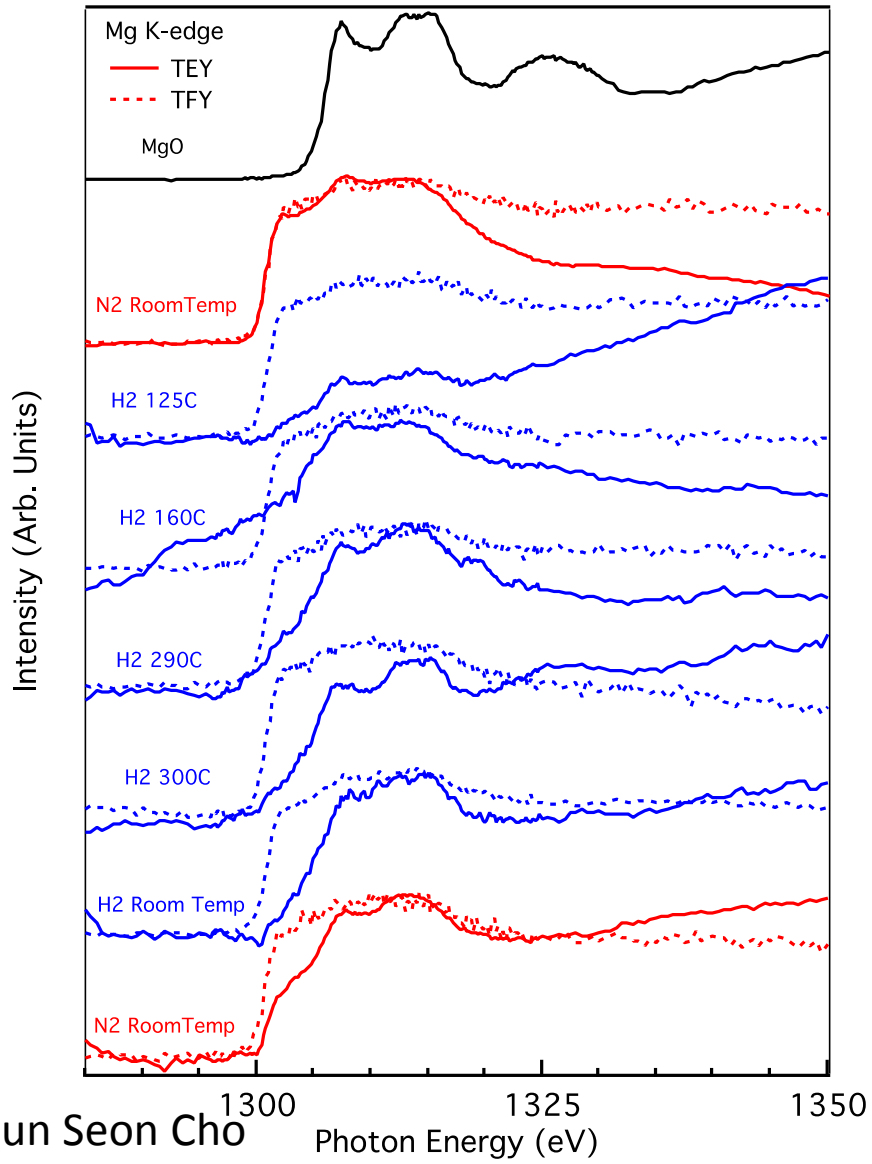


Co Catalysts: NL (2011), JACS (2013)



Jinghua Guo and Yi-Sheng Liu

In-situ Characterization of Mg NPs@Graphene



Samples: Jeff Urban and Eun Seon Cho

XAS measurements: Jinghua Guo and Yi-Sheng Liu

XAS interpretation (TBD): Prendergast

First-principles simulations of X-ray Absorption

Density functional theory

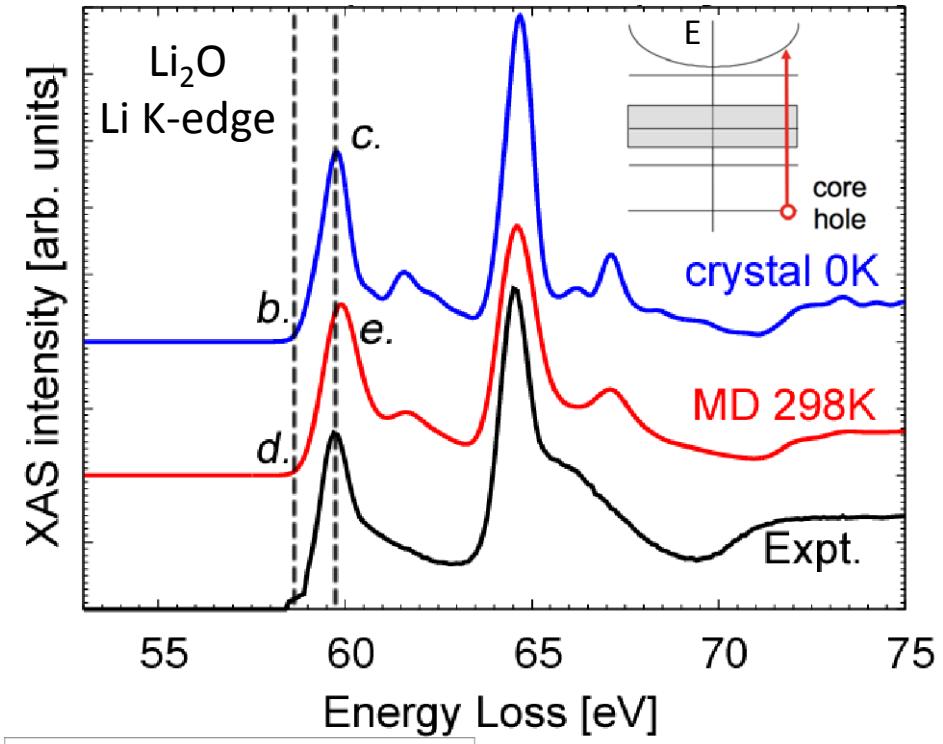
- constrained excited state (core-hole)
- include excited electron
- Fermi's Golden Rule for XAS

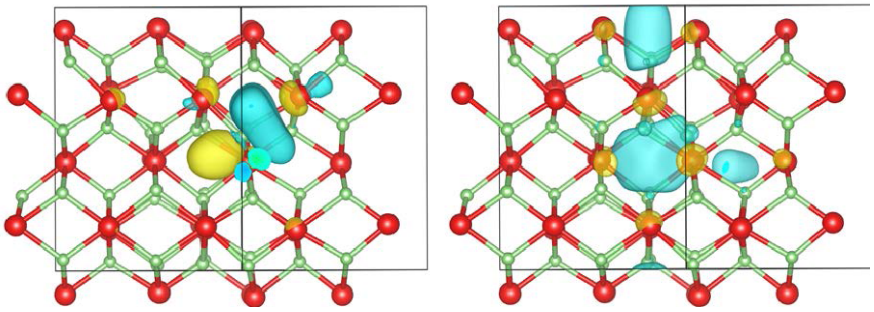
$$\sigma(\omega) = 4\pi^2 \alpha_0 \hbar\omega \sum_f^{unocc} |\langle \Psi_f | \epsilon \cdot r | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

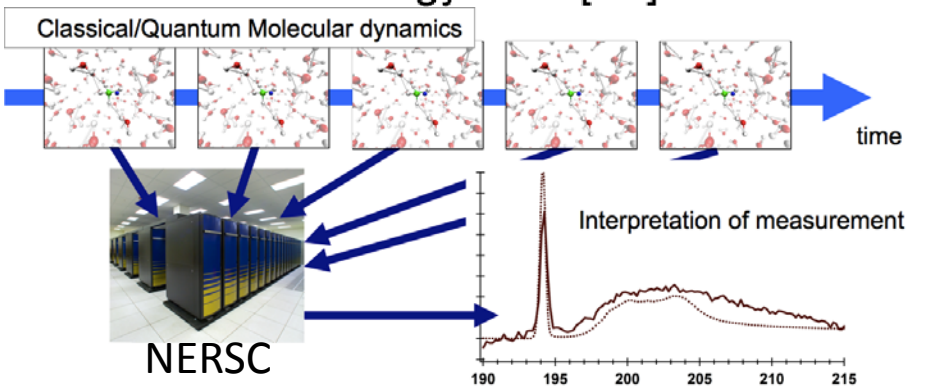
- inclusion of finite temperature (dynamics)
- accurate energy alignment
- correct description of defects

Predictive method for unknown/mixed phases

- explore dopants (e.g. Ti)
- solid-solid interfaces/surface chemistry
- interpretation of in-situ studies





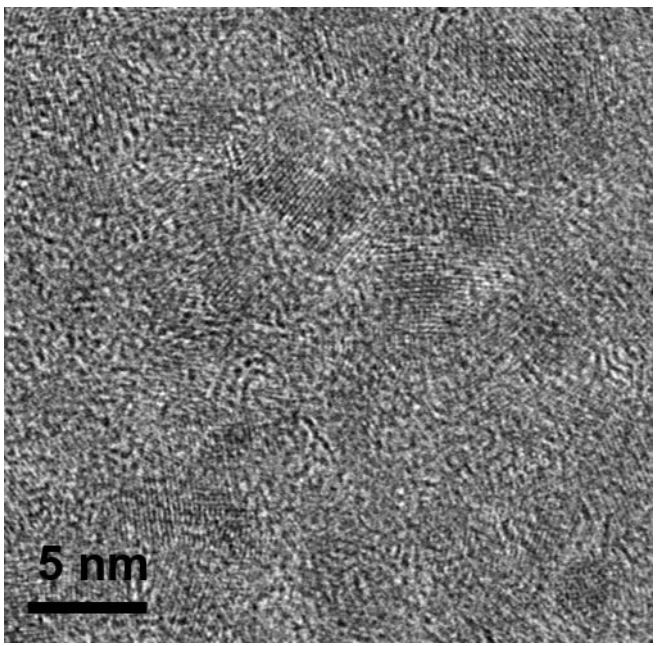


Theory: David Prendergast, Craig Schwartz, Jan Aeschlimann, Sabrina Wan

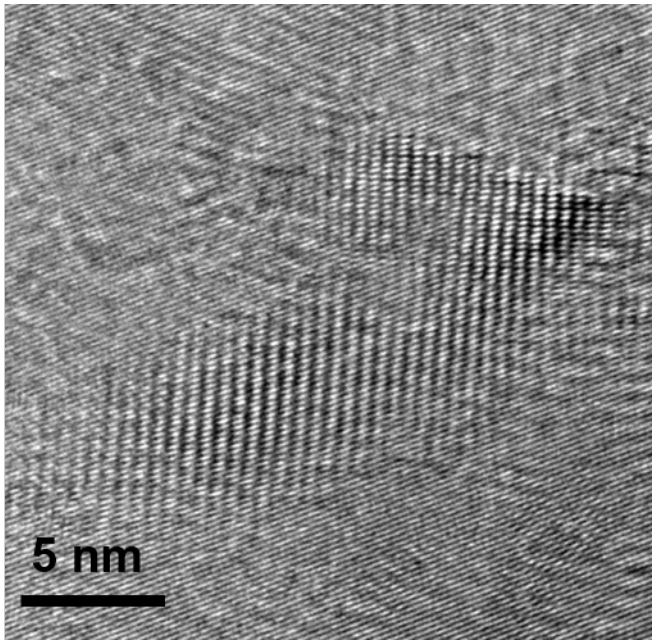
Milestone: Controlled Nanoscale Hydrides

Mg nanocrystals

< 5nm | 5-10 nm | > 10 nm



5-10nm: Not yet completed

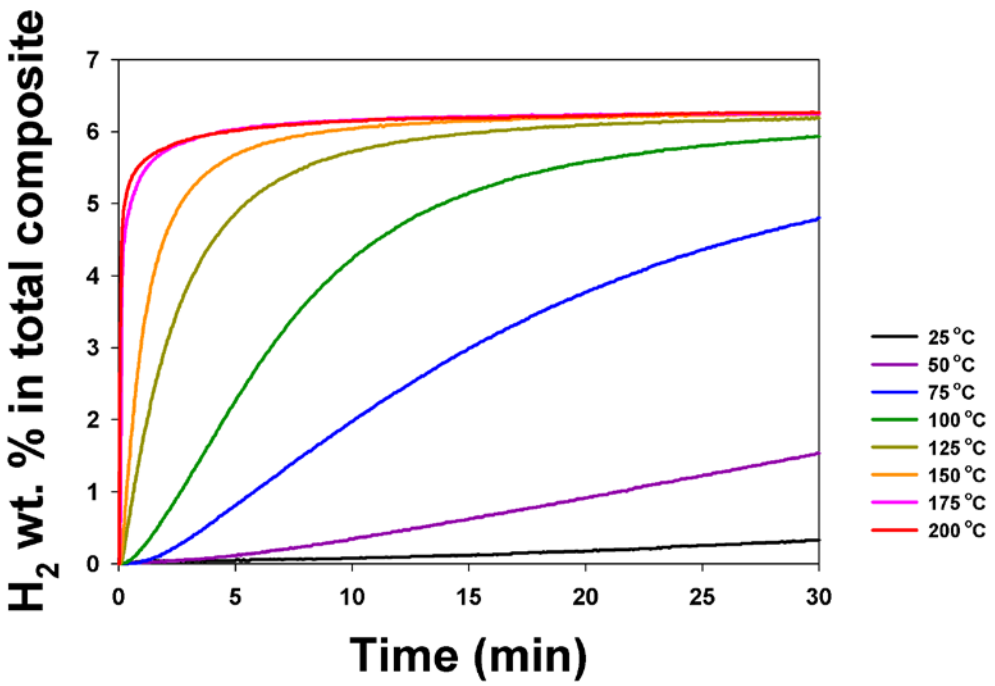


(1) E. Cho, A. M. Ruminski, S. Aloni, Y-S. Liu, J. Guo, J. J. Urban, *Nature Comms* (2016).

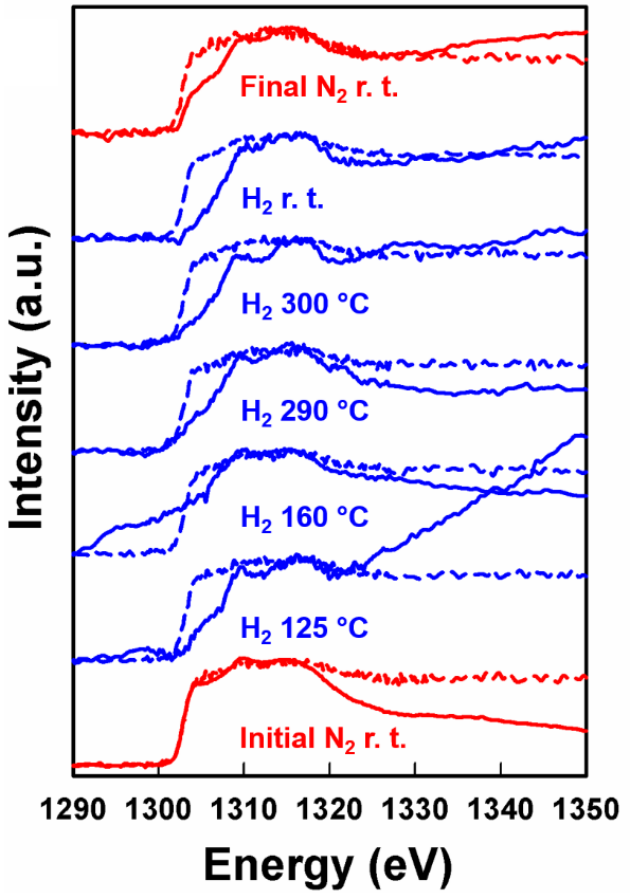
Accomplishment: Hydrogen Sorption for Ni-Doped rGO-Mg

Ni-dopant is most efficient and reproducible for hydrogen sorption (Task 4&5)

Hydrogen absorption at different temperatures with 15 bar of H_2



In-Situ XANES upon 1 bar of H_2 with temperature ramping



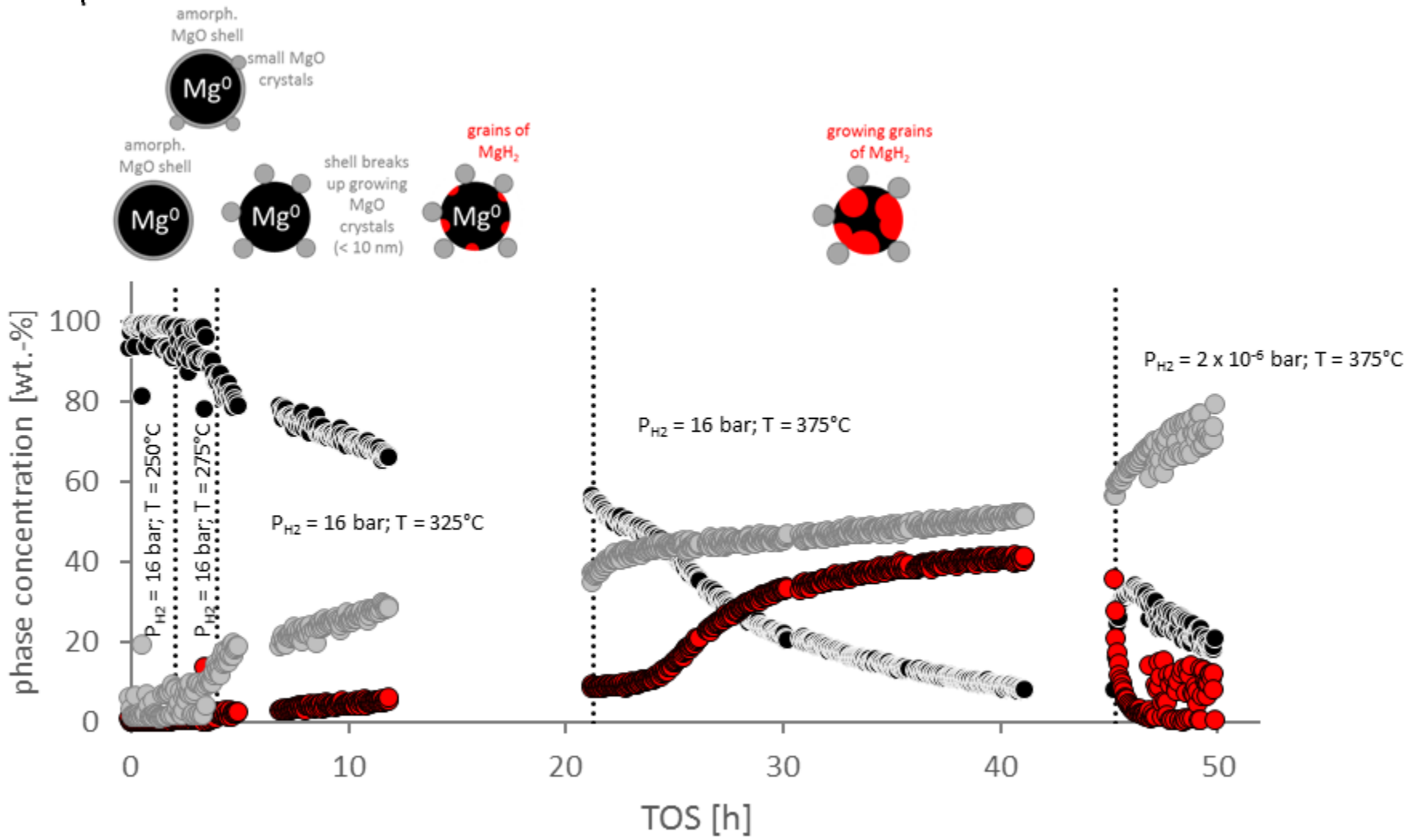
Ni-doped rGO-Mg is fairly reproducible in further cycles with highly enhanced kinetics.

Collaboration with Jinghua Guo & Yi-Sheng Liu

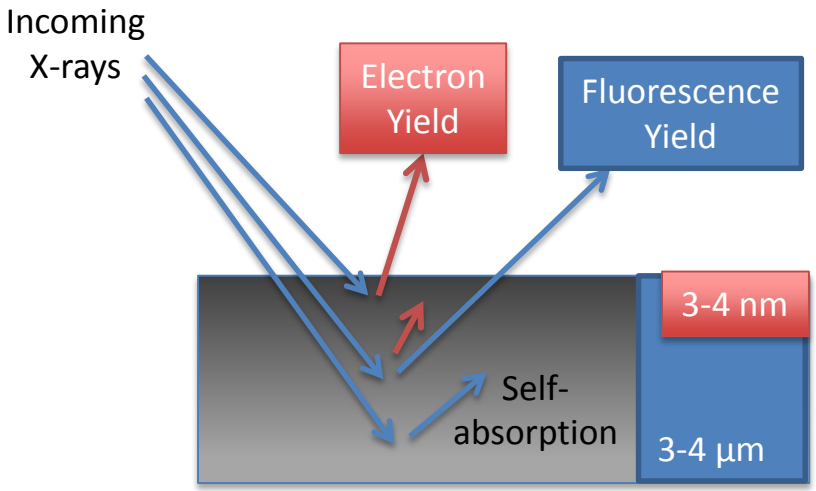
(1) E. Cho, A. M. Ruminski, Zhou, X., Wood, B, Y-S. Liu, J. Guo, J.J. Urban, *in preparation*.

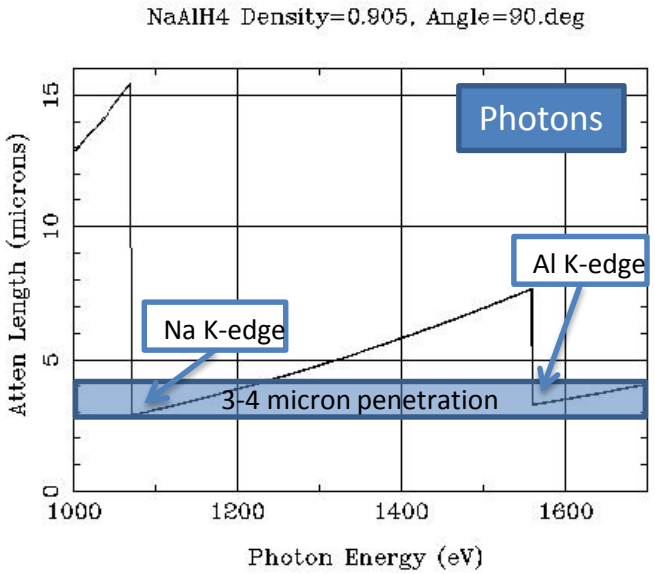
Accomplishment: Initial work on in situ XRD characterization

- A direct characterization of phase transformation of Mg to MgH_2 under performance relevant conditions has been initiated. Further optimization and method development is required.

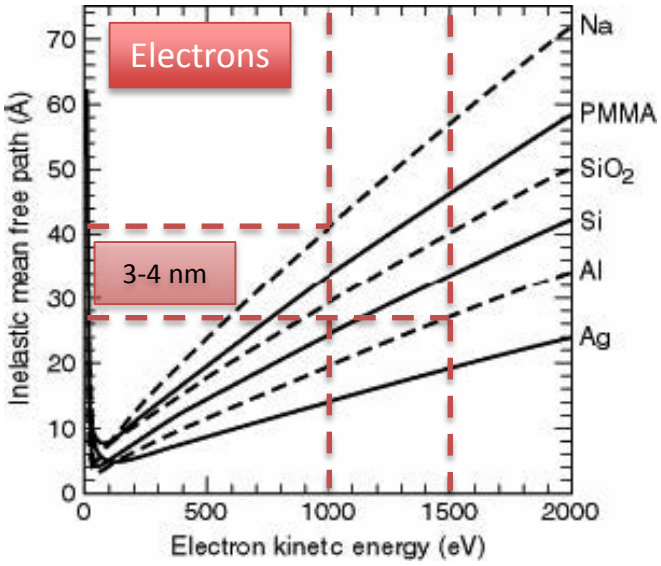


Surface vs. Bulk exploration using X-ray Absorption Spectroscopy at the ALS

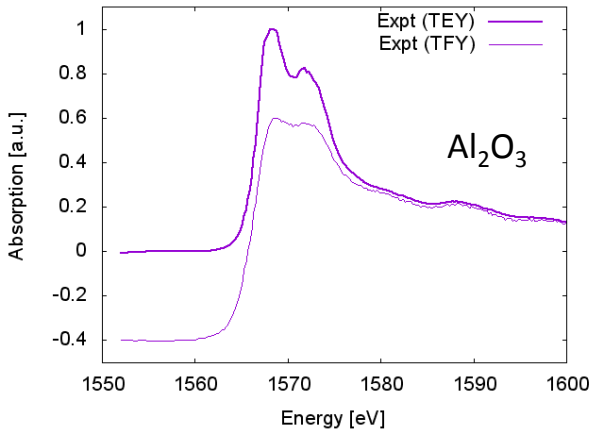


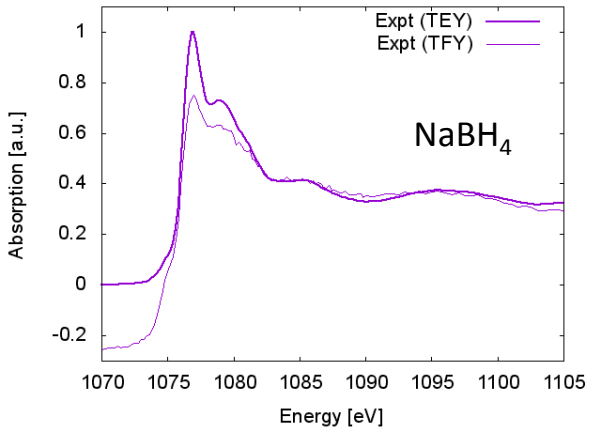


http://henke.lbl.gov/optical_constants/atten2.html



http://xdb.lbl.gov/Section3/Sec_3-2.html

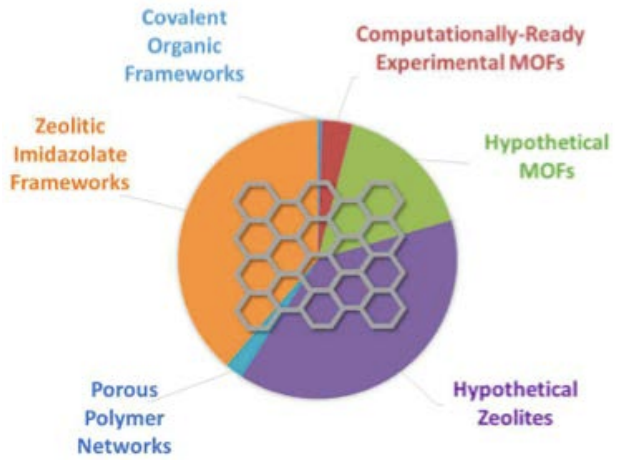


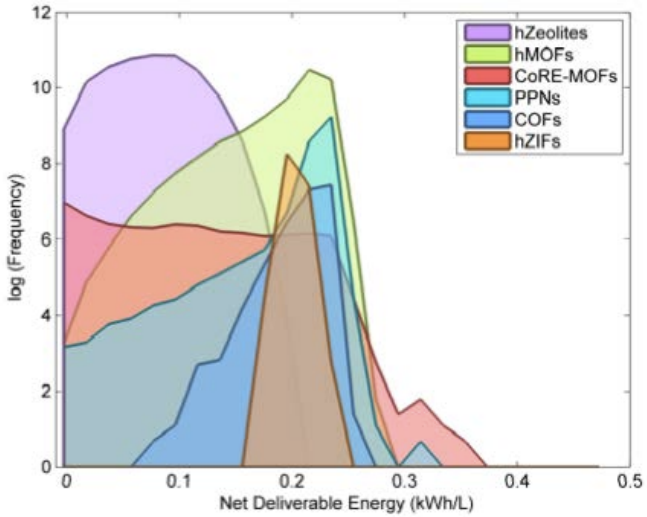


Self-absorption can "erode" sharp peaks at absorption onset in TFY

Screening Sorbents Materials

A Materials Genome Approach





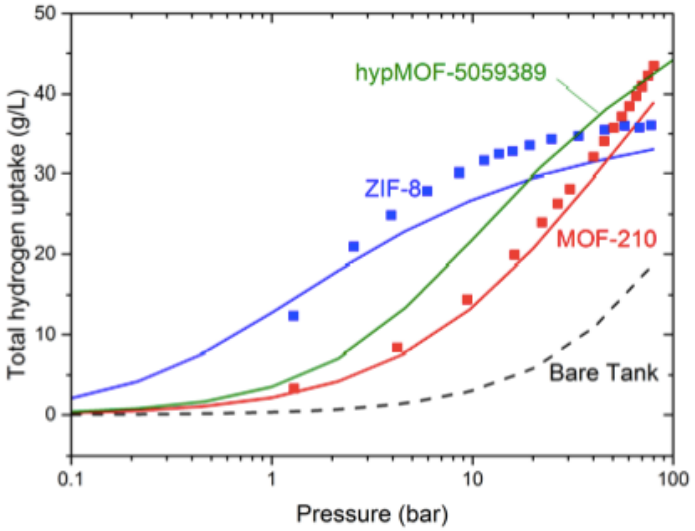
A set of ca. 850000 porous materials of various classes was screened to identify materials with highest hydrogen storage performance

- Screening was done by a hybrid simulation-statistical learning approach, where performance of each material was predicted using a neural network model based on structure descriptors (provided by our Zeo++ code)
- Molecular simulations were used to characterize adsorption (working capacity between 100 and 1 bar) for materials used to train the NN model
- Grand Canonical Monte Carlo simulations were done at 77K, using classical UFF potential for framework atoms and Bush potential for hydrogen

(1) Thornton, A. et al. EES submitted.

HyMARC BERKELEY LAB

Storage in Strong Hydrogen-Binding MOFs



- Classical Grand Canonical Monte Carlo simulations can be used to predict adsorption isotherms
- Investigation of systems, which include Open Metal Sites (OMS) and are expected to have high hydrogen-material interaction energy require specially derived interatomic potentials
- Together with Task 1, we are analyzing the CORE MOF database to identify representative MOF materials with OMS
- Together with Task 5, we will employ Quantum Monte Carlo techniques to study H2-MOF interactions In those materials and derive refined class-transfarable potentials for use in GCMC simulations

(1) Thornton, A. et al. EES submitted.