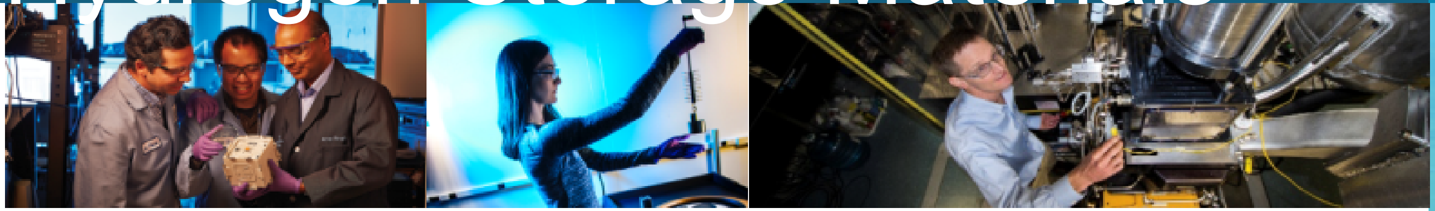
SAND2020-11814C

Challenges and Opportunities for Soft X-ray Characterization of Hydrogen Storage Materials



The Advanced Light Source
2020 RIXS group retreat outreach forum
Friday, Oct 30th, 2020

Jonathan L. Snider, Alexander A. Baker, Farid El Gabaly, Vitalie Stavila, Mark D. Allendorf

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Outline

- Introduction to HyMARC
- Examples of insights gained from soft X-ray XAS
- Materials challenges and needs
- Opportunities for in-situ experiments
- Opportunities for X-ray imaging
- Summary

Research a HyMARC

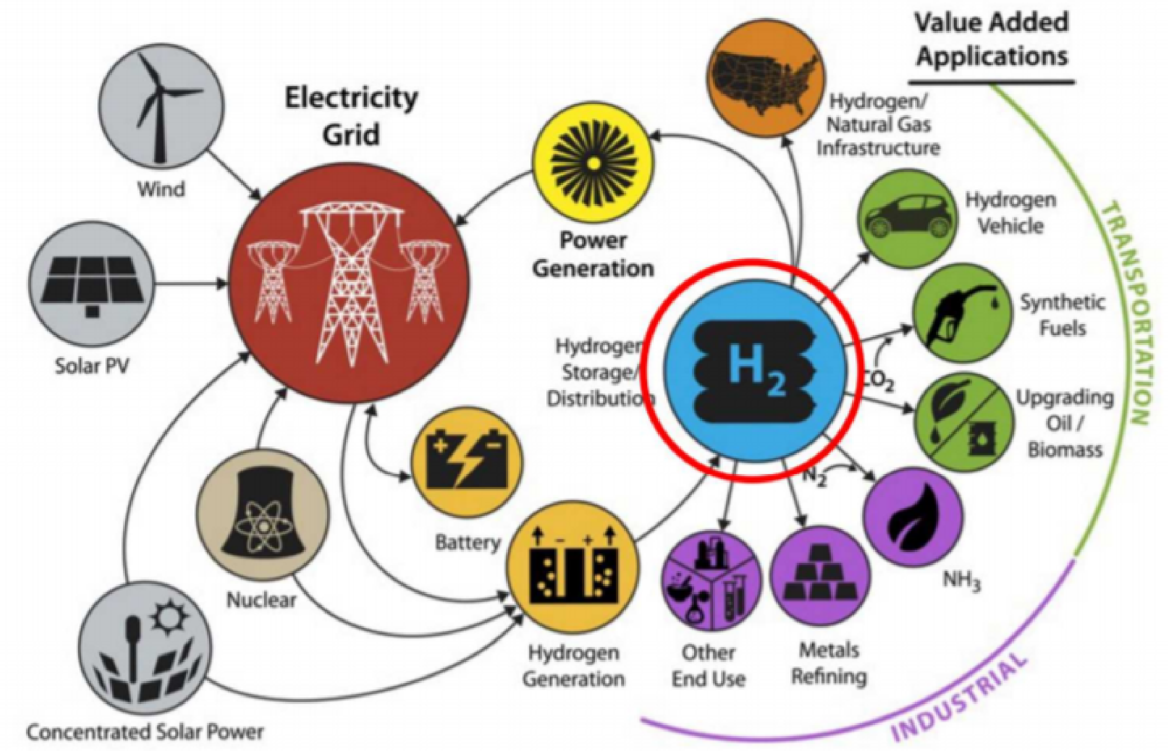
Hydrogen Materials Advanced Research Consortium

- HyMARC seeks to enable the H2@Scale concept by developing new concepts and materials that provide advantages for the transportation and storage of H_2

- Research efforts include sorbents, metal hydrides, and hydrogen carriers
  - These materials can provide high density storage and transportation of hydrogen
  - Research is needed to improve reversible capacities and enable milder cycling conditions

- Soft X-ray characterization is needed to understand the chemistry of hydrogen storage materials containing light elements

H2@Scale concept

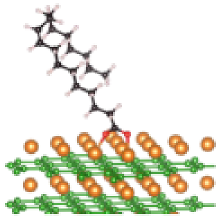


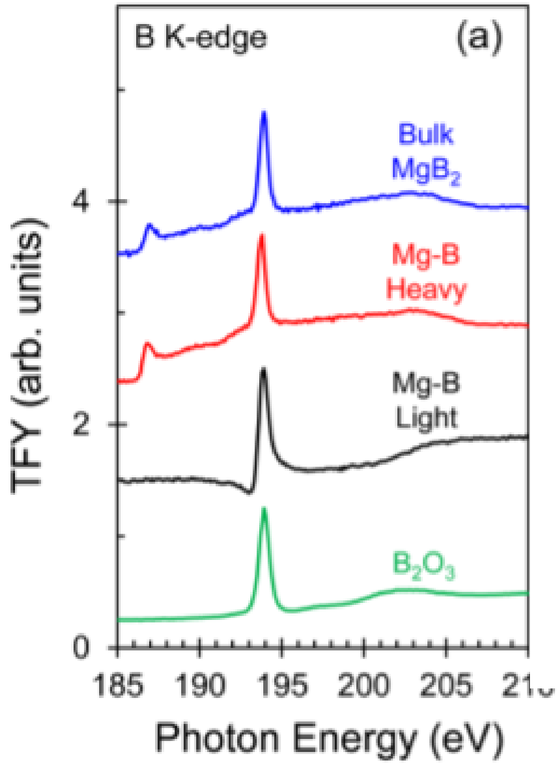
https://www.energy.gov/eere/fuelcells/h2scale

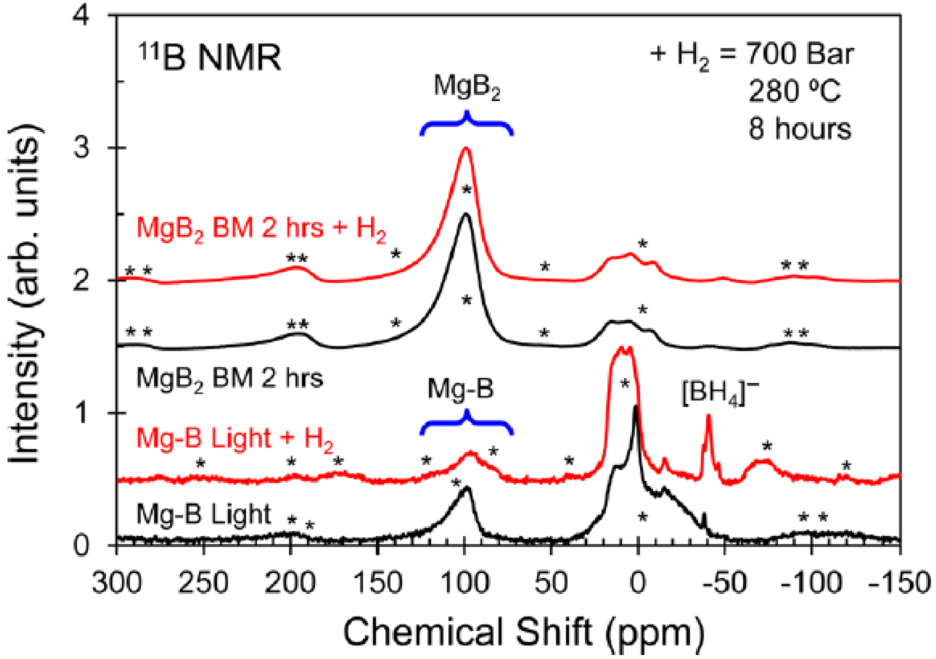
What have we learned from soft X-ray XAS?

Nanoscale Mg−B *via* Surfactant Ball Milling of MgB_2: Morphology, Composition, and Improved Hydrogen Storage Properties

Y.-S. Liu, K. G. Ray, M. Jørgensen, T. M. Mattox, D. F. Cowgill, H. V. Eshelman, A. M. Sawvel, J. L. Snider, W. York, P. Wijeratne, A. L. Pham, H. Gunda, S. Li, T. W. Heo, S. Kang, T. R. Jensen, V. Stavila, B. C. Wood, and L. E. Klebanoff*







- Nanoscale Mg-B was produced via surfactant ball milling of MgB_2
- B K-edge XAS reveals that the nanoscale "Light" fraction has a disrupted B-B ring
  - The unoccupied B $2p_{xy}$ feature at ~187 eV is absent
- The nanomaterial has significantly improved hydrogenation activity:
  - $Mg(BH_4)_2$ is formed at 700 bar H_2 and 280 ºC with the "Light" fraction
  - Ball-milled MgB_2 requires 950 bar and 400 ºC to hydrogenate

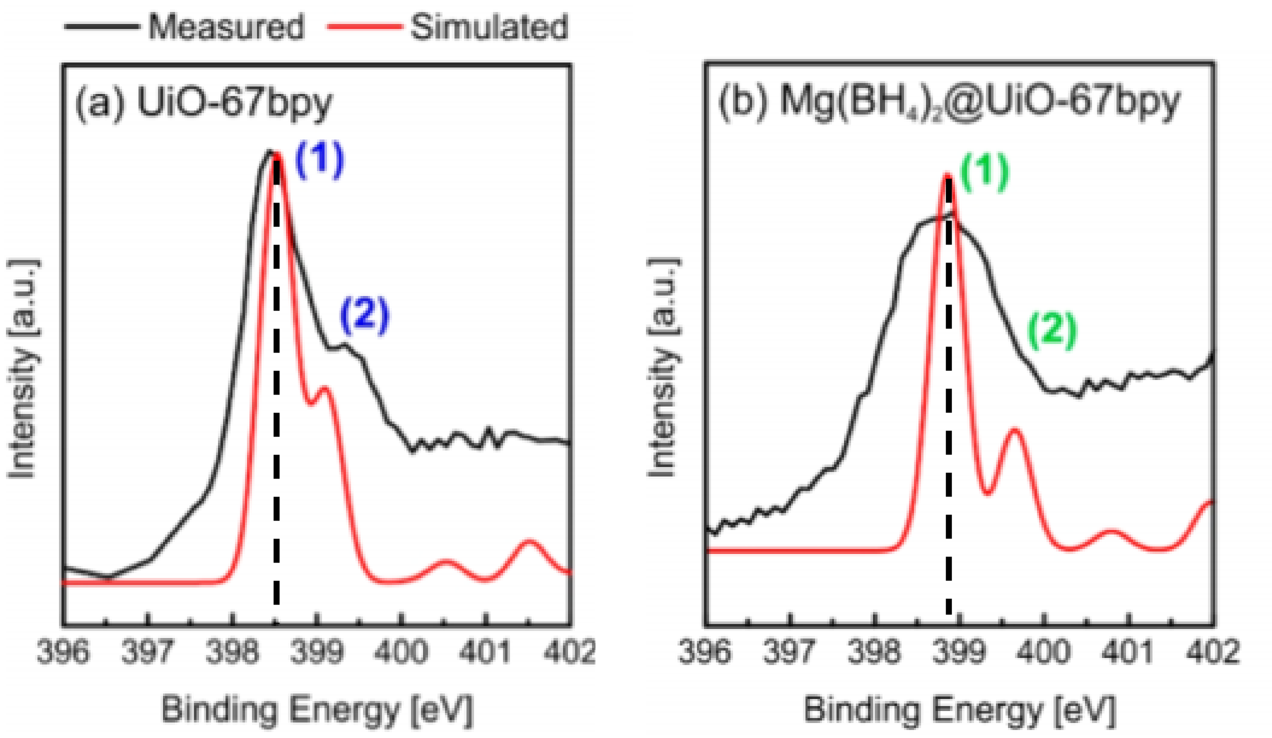
XAS reveals a disruption of the B-B ring which helps to destabilize MgB_2 and promote hydrogenation performance

Liu, Y.-S., et al. *J. Phys. Chem. C,* 2020, **124**,

What have we learned from soft X-ray XAS?

Nanoconfinement of Molecular Magnesium Borohydride Captured in a Bipyridine-Functionalized Metal–Organic Framework

Andreas Schneemann, Liwen F. Wan, Andrew S. Lipton, Yi-Sheng Liu, Jonathan L. Snider, Alexander A. Baker, Joshua D. Sugar, Catalin D. Spataru, Jinghua Guo, Tom S. Autrey, Mathias Jørgensen, Torben R. Jensen, Brandon C. Wood, Mark D. Allendorf,* and Vitalie Stavila*



- A bipyridine-functionalized UiO-67 framework was used to capture molecular $Mg(BH_4)_2$
  - Nanoconfinement lowers the onset of hydrogen desorption by ~150 °C
- The $Mg(BH_4)_2$ is found to bind at the pyridinic nitrogen in UiO-67bpy
  - XAS at the N k-edge reveals a shift to higher binding energy, consistent with simulations of $Mg(BH_4)_2$ bound to H_2bpydc

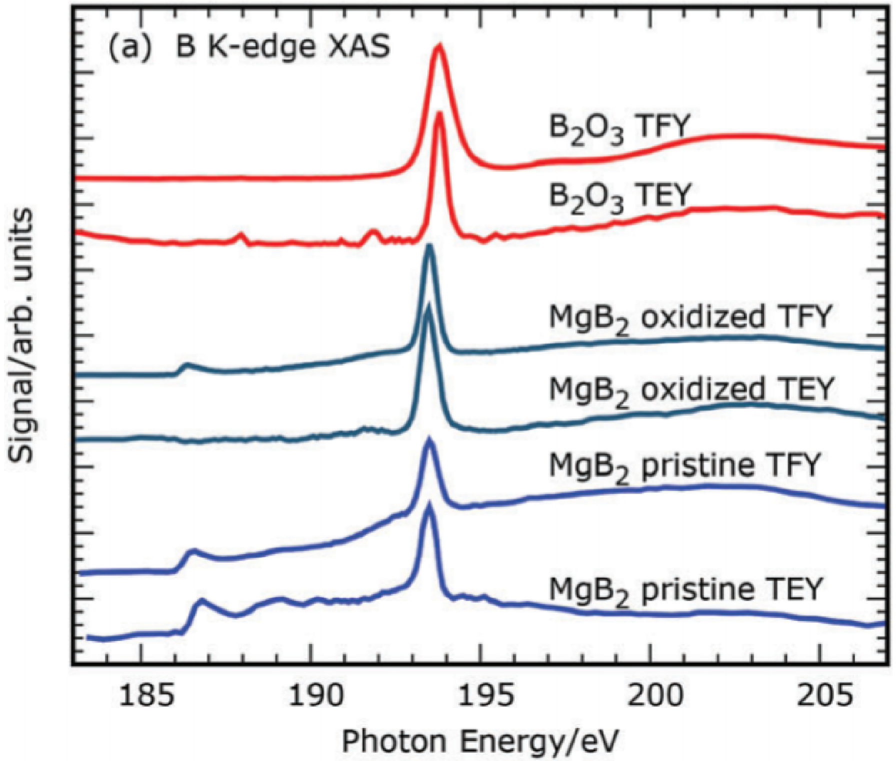
Characterization of hosts can reveal their interactions with confined hydrogen storage materials

Schneemann, A., et al. *ACS Nano*, 2020, **14**, 10294-10304

Challenges in handling air-sensitive materials

Elucidating the mechanism of MgB_2 initial hydrogenation *via* a combined experimental–theoretical study†

Keith G. Ray,[a] Leonard E. Klebanoff,*[b] Jonathan R. I. Lee,[a] Vitalie Stavila,[b] Tae Wook Heo,[a] Patrick Shea,[a] Alexander A. Baker,[a] Shinyoung Kang,[a] Michael Bagge-Hansen,[a] Yi-Sheng Liu,[c] James L. White[b] and Brandon C. Wood[a]



- **Safety:** Many hydrogen storage materials are <u>pyrophoric</u>
  - Metal hydrides (e.g. AlH_3, $NaAlH_4$)
  - Metal borohydrides (e.g. $Mg(BH_4)_2$)
  - Metal nitrides/amides (e.g. Li_3N)
- Upon oxidation, surface features are lost and signal can be dominated by the oxidized species, as shown for MgB_2 to the left.
- Even trace amounts of O_2 or H_2O can lead to oxidation, as shown in "pristine" MgB_2 measurements
  - Care must be taken to remove all oxygen sources from the handling and transfer setup
  - N_2 plastic bag transfers and dry-air glove-boxes are insufficient

Air-free transfer is necessary for the handling of most hydrogen storage materials

Ray, K.G., et al. *Phys. Chem. Chem. Phys.* 2017, **19**, 22646

Continued need for low energy soft X-ray XAS HyMARC

Nanoconfined metal amides

Achieving low-cost hydrogen storage by tuning the desorption thermodynamics of the Li-Mg-N-H system with composition tuning and nanoconfinement

Research Question:
- How do composition tuning and nanoconfinement change the electronic structure and reactivity of the Li-Mg-N-H system?
- **Elements:** Li, Mg, N, C

Research Question:
- How do dopants interact with the Li-Mg-N-H system?
- **Elements:** N, K

Research Question:
- How does the composite material change upon cycling?
- **Elements:** Li, Mg, N, K, C

Seedling project support

Promotion of MgB_2 to enable reversible hydrogen storage under milder conditions (G. Severa)

Research Question:
- How do additives change the electronic structure of MgB_2?
- **Elements:** B, Mg, C

Evaluating the hydrogen storage performance of AlC_x and BC_x (N. Stadie)

Research Question:
- How do synthesis conditions change B-C and Al-C bonding?
- **Elements:** B, Al, C

Opportunities for in-situ experiments

Heating

- Heating samples to observe species present during dehydrogenation reactions
- Temperatures up to 400 °C will accommodate most materials
- For example, AP-XPS revealed the role of surface hydroxide species that form during dehydrogenation of Ti-doped $NaAlH_4$ (figure to the right)

Increased environmental control

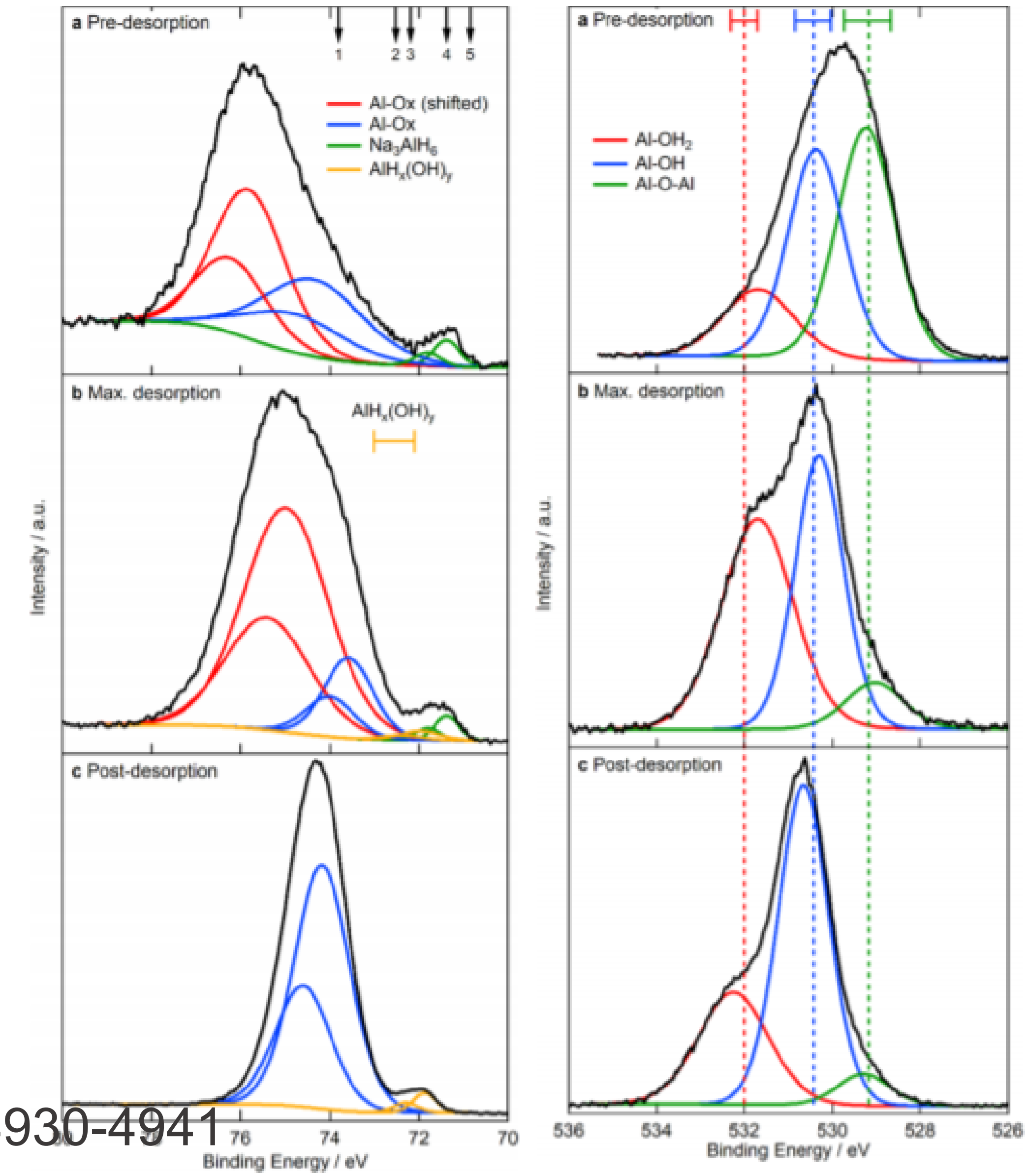
- Access to a wider range of supplied H_2 gas pressures (>1 bar) enables study of more hydrogenation reactions

Characterization of evolved gas

- Determination of evolved species during dehydrogenation
- Particularly relevant for the study of metal amides which can evolve ammonia (undesired reaction)

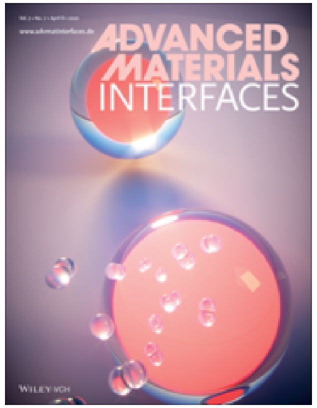
Identifying the Role of Dynamic Surface Hydroxides in the Dehydrogenation of Ti-Doped $NaAlH_4$

James L. White,[†] Andrew J. E. Rowberg,[‡,§] Liwen F. Wan,[‡,∥] ShinYoung Kang,[‡] Tadashi Ogitsu,[‡] Robert D. Kolasinski,[†] Josh A. Whaley,[†] Alexander A. Baker,[‡] Jonathan R. I. Lee,[‡] Yi-Sheng Liu,[∥] Lena Trotochaud,[∥] Jinghua Guo,[∥] Vitalie Stavila,[†] David Prendergast,[∥] Hendrik Bluhm,[∥] Mark D. Allendorf,[†] Brandon C. Wood,[*,‡] and Farid El Gabaly[*,†]



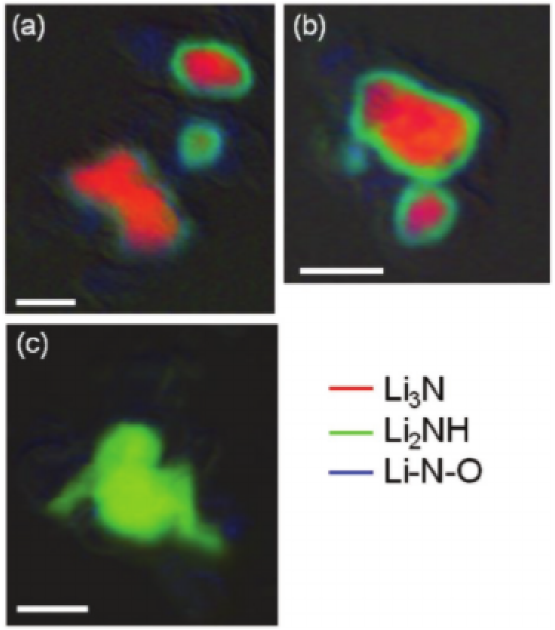
White, J.L., et al. *ACS Appl. Mater. Interfaces*, 2019, **11**, 4930-4941

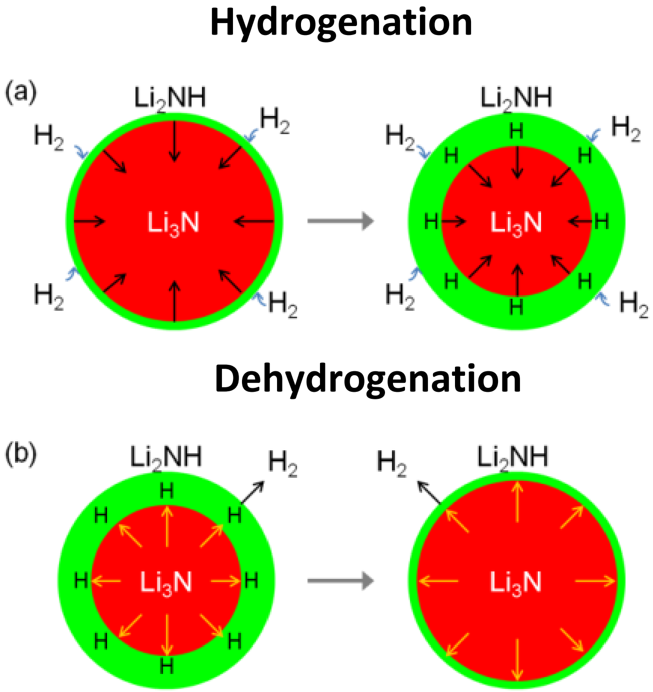
Opportunities for imaging microstructures



The Inside-Outs of Metal Hydride Dehydrogenation: Imaging the Phase Evolution of the Li-N-H Hydrogen Storage System

*James L. White, Alexander A. Baker, Matthew A. Marcus, Jonathan L. Snider, Timothy C. Wang, Jonathan R. I. Lee, David A. L. Kilcoyne, Mark D. Allendorf, Vitalie Stavila, and Farid El Gabaly**





- STXM was performed to determine the phase evolution of the Li-N-H system
- A core-shell structure is observed, with a hydrogen-rich shell forming in both the hydrogenation and dehydrogenation reactions
- Results reveal the reaction mechanisms for these materials and help guide modeling efforts
  - Additional data on more system is desired to advance the models further

With image resolutions of <50 nm, microstructural models of hydrogen storage materials can be advanced

White, J.L., et al. *Adv. Mater. Interfaces*, 2020, **7**, 1901905

Summary

The use of soft X-ray capabilities at the ALS has yielded tremendous insights into the chemistry of hydrogen storage materials, resulting in numerous publications

The study of hydrogen storage materials can be advanced significantly by further developments in soft X-ray characterization:

- Development of low energy capabilities empower the study of systems involving **Li** and **B**
- Air-free transfer setups are needed for any instrument measuring pyrophoric materials
- In-situ experiments require heating up to 400 ºC and gas pressure (e.g. >1 bar H_2)

Acknowledgements

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  - **SNL**: Mark Allendorf, Vitalie Stavila, Leonard Klebanoff, Farid El Gabaly, James White, Andreas Schneemann, …
  - **LLNL**: Alexander Baker, Jonathan Lee, Brandon Wood, Keith Ray, Tae Wook Heo, Shinyoung Kang, Liwen Wan, …
  - **LBNL**: Jinghua Guo, Yi-Sheng Liu, Matthew Marcus, David Kilcoyne, Hendrik Ohldag, David Prendergast, …

Thank you for your attention!