SAND2018-8177PE

Role of Surface Oxidation in the Dehydrogenation of Complex Metal Hydrides

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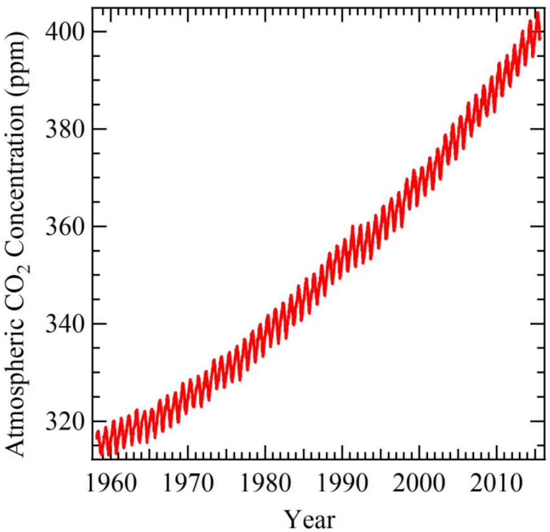
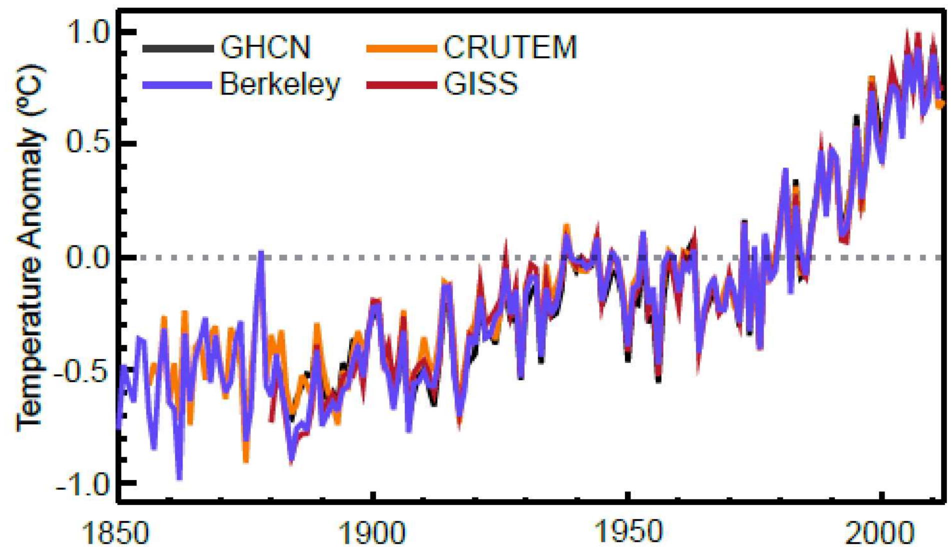
Anthropogenic Climate Change





IPCC Fifth Assessment Report, 2013

Shift from Fossil to Renewable Energy

Storage as Hydrogen

- High gravimetric energy density
  - 1 kg H_2 equivalent to 3 kg (1 gallon) gasoline
- Very low volumetric energy density
  - >3000 gallons H_2 (STP) equivalent to 1 gallon gasoline

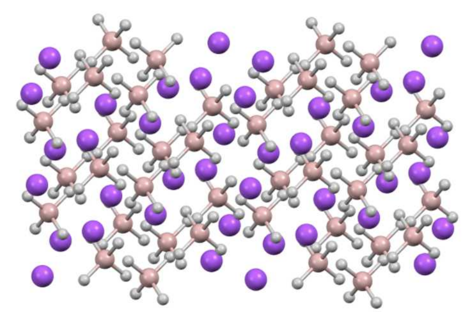
Compress

40 kg H_2 m^{-3} at 700 bar

Liquefy

70 kg H_2 m^{-3} at 21 K

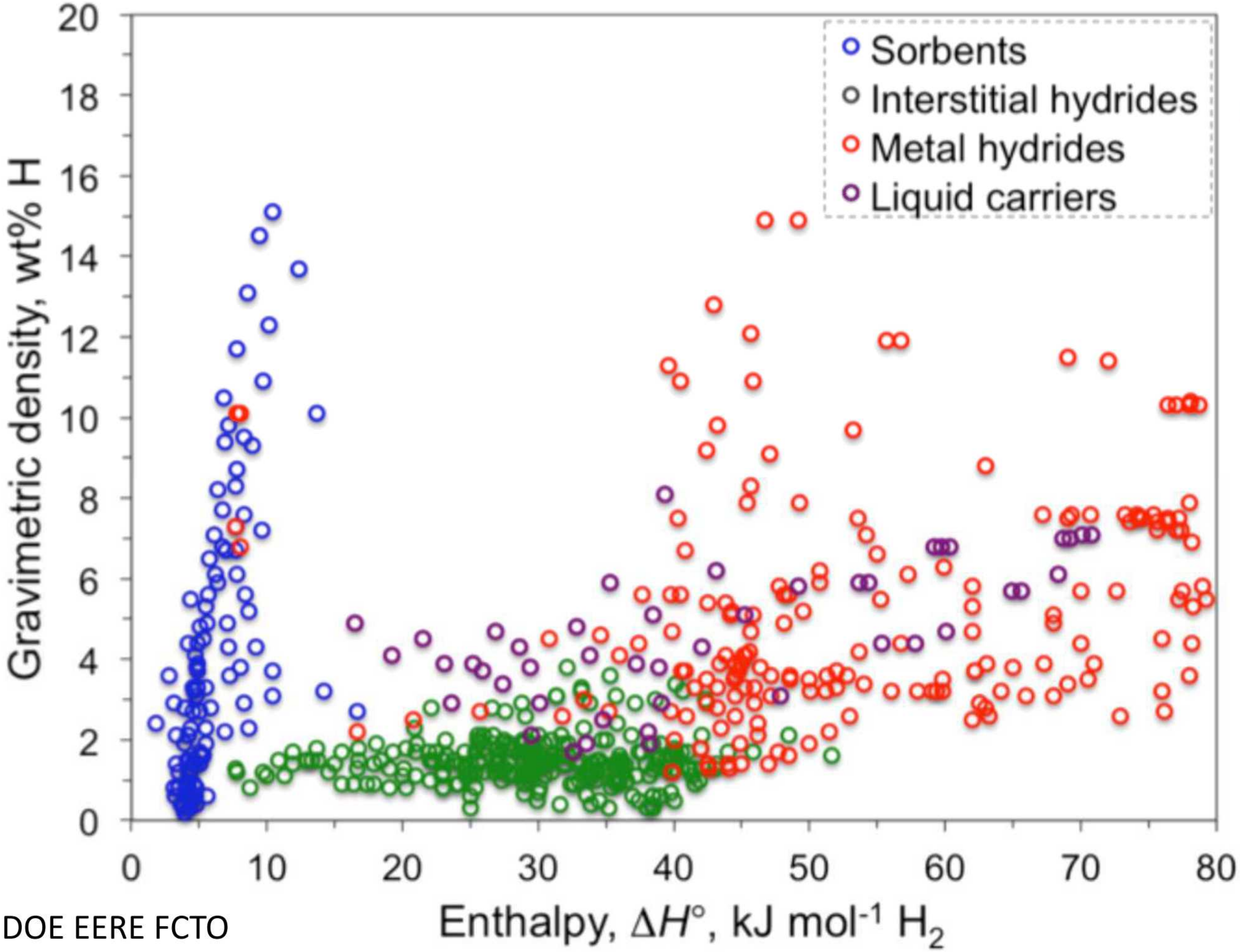
Solidify



Dias et al., Science 355, 715 (2017)

Up to 150 kg H_2 m^{-3} at RT in metal hydrides

Vehicular Hydrogen Storage Goals



DOE EERE FCTO

- DOE 2020 System Targets
  - 5.5 wt% H_2
  - 40 g H_2 / L
  - 85° C max delivery temp. (ΔH≈20-30 kJ/mol H_2)
  - Reversible (1500 cycles)
  - 1.5 kg H_2 / min fill rate

Need "Goldilocks" thermochemical properties and fast kinetics!

HyMARC
Hydrogen Materials Advanced Research Consortium
https://hymarc.org/

Sandia National Laboratories
Lawrence Livermore National Laboratory
BERKELEY LAB
Lawrence Berkeley National Laboratory

Three Bay Area DOE National Laboratories serve as core team

Goals

"Foundational understanding, synthetic protocols, new characterization tools, and validated computational models" for solid-phase hydrogen storage materials to meet industry requirements for vehicles

Sorbents	Bulk Hydrides	Nanostructured Hydrides

Sodium Aluminum Hydride

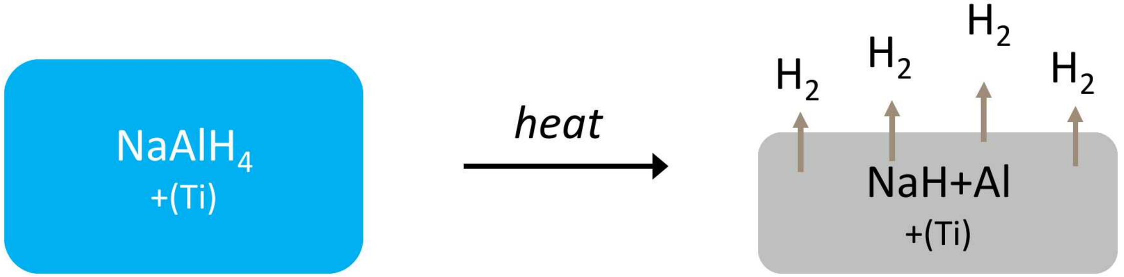
$<200\ ^\circ C$ $\quad 3\ NaAlH_4 \rightleftharpoons Na_3AlH_6 + 2\ Al + 3\ H_2$

$\sim 250\ ^\circ C$ $\quad Na_3AlH_6 \rightleftharpoons 3\ NaH + Al + {}^{3}/_{2}\ H_2$

$>400\ ^\circ C$ $\quad 3\ NaH \rightarrow 3\ Na + {}^{3}/_{2}\ H_2$

$+\ TiCl_3$

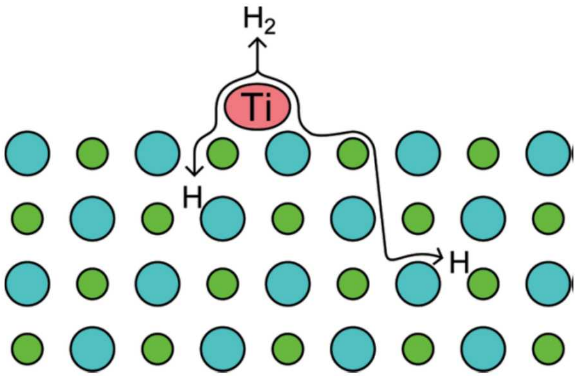
Effective capacity of 5.6 wt.% H



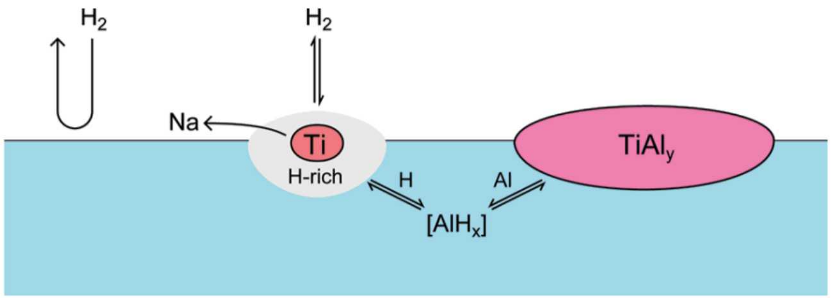
What **form** of Ti is present and what is its **role** in (de)hydrogenation at the surface?

J. Alloys Compd. **1997**, *253–254*, 1-9.
Chem. Rev. **2012**, *112*, 2164-2178.

Ti-Doped $NaAlH_4$-Prior Predictions



Metallic Ti on surface acts as H_2 pump or spillover site

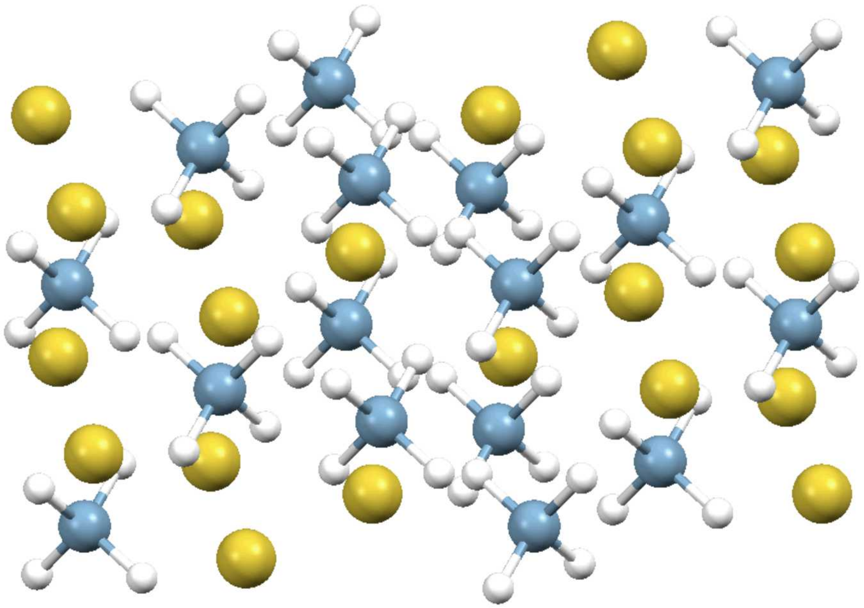


Ti alloys with Al and encourages Na vacancies while bringing H atoms together

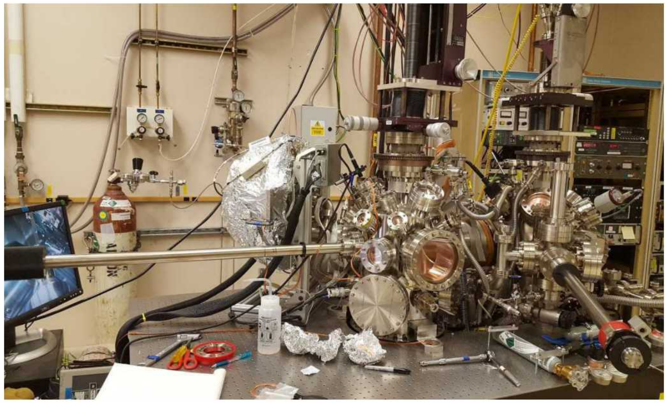
Chem. Rev. **2012**, *112,* 2164-2178.

Sample Preparation

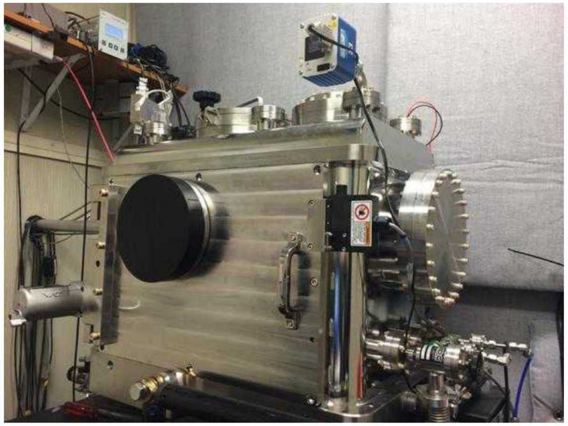
- Recrystallized $NaAlH_4$ from diethyl ether
- Ball-milled in 0.4, 2, and 10 mol% $TiCl_3$
- Cycled three times by desorbing at 200 °C and rehydrogenating at 150 °C and 100 bar H_2



Major Characterization Techniques

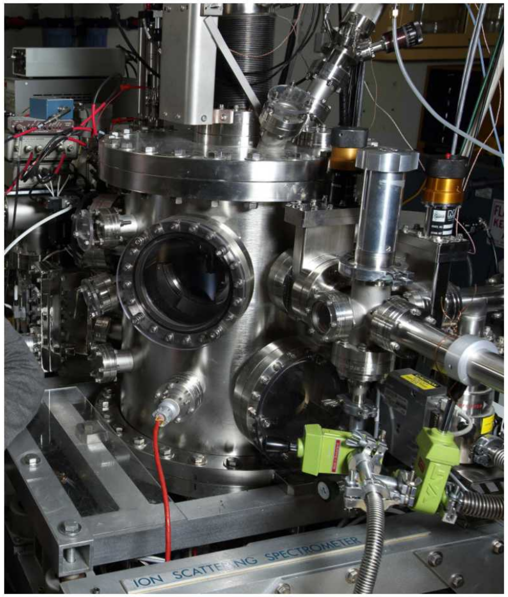


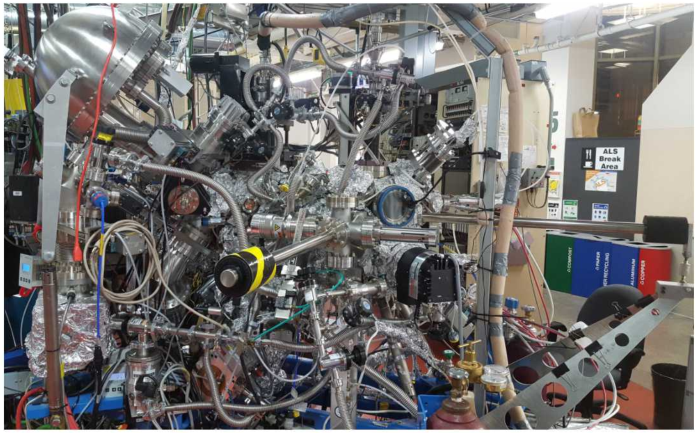
X-ray Photoelectron Spectroscopy (XPS)



Scanning Transmission X-ray Microscopy (STXM) at BL5.3.2.2

Low Energy Ion Scattering (LEIS)

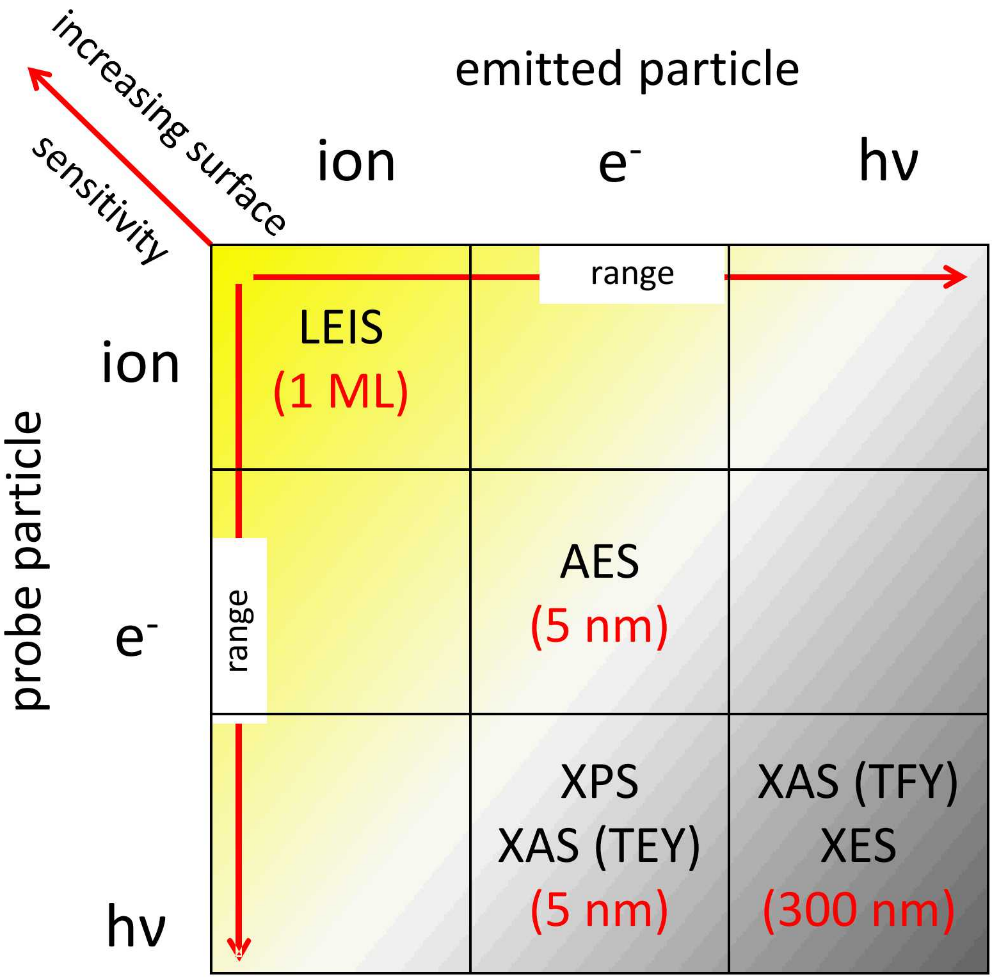


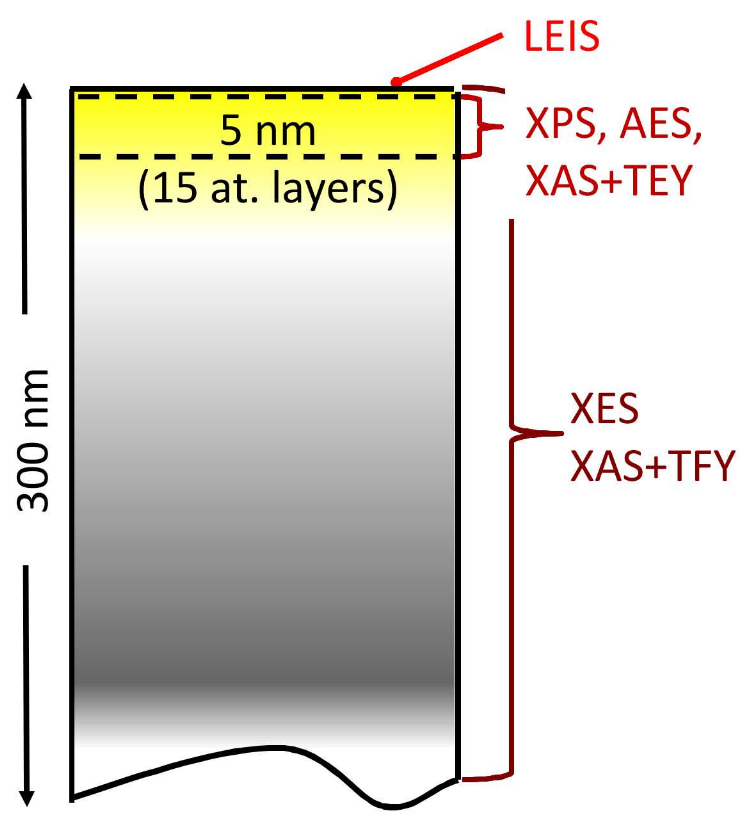


Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at BL11.0.2

Others: X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD)

Surface Sensitivity of Probes: Information depth depends on particle range

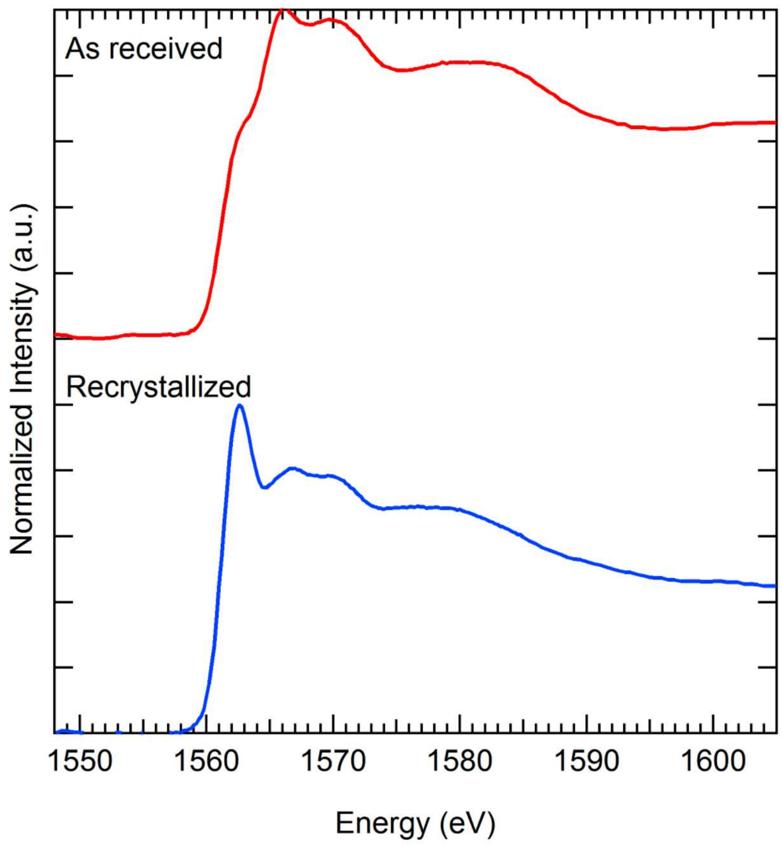


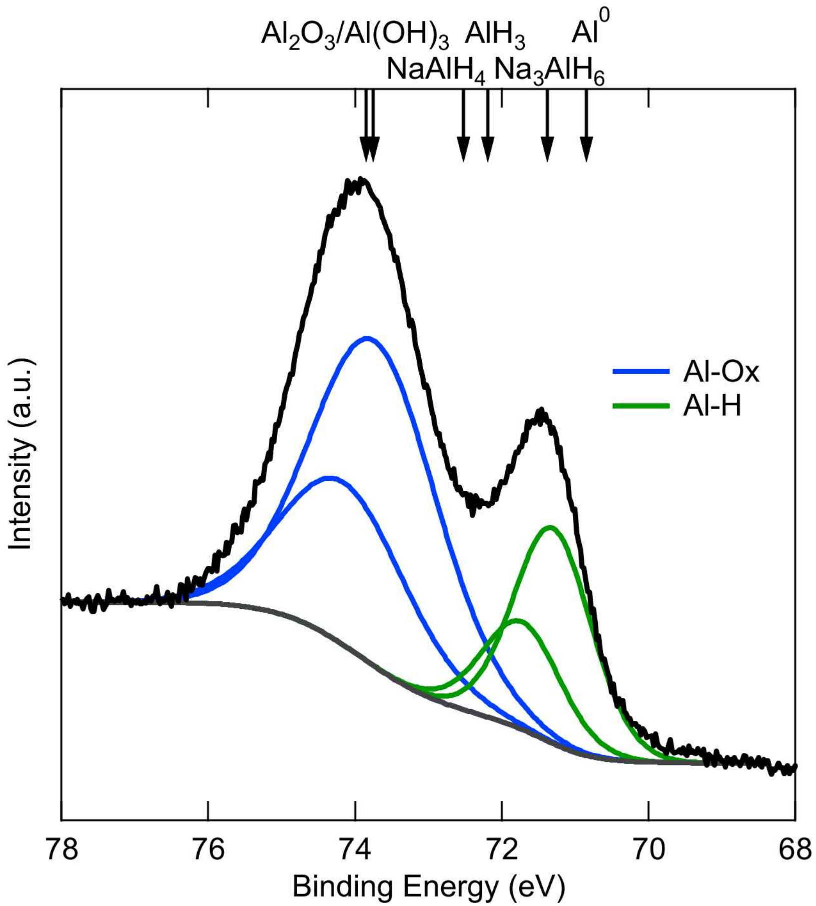


TFY: total fluorescence yield

TEY: total electron yield

Recrystallized $NaAlH_4$

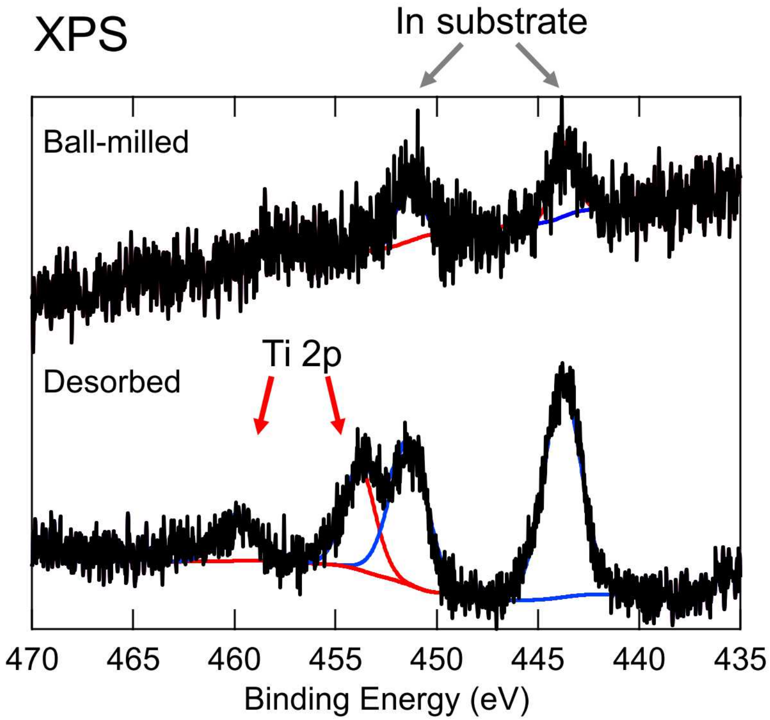




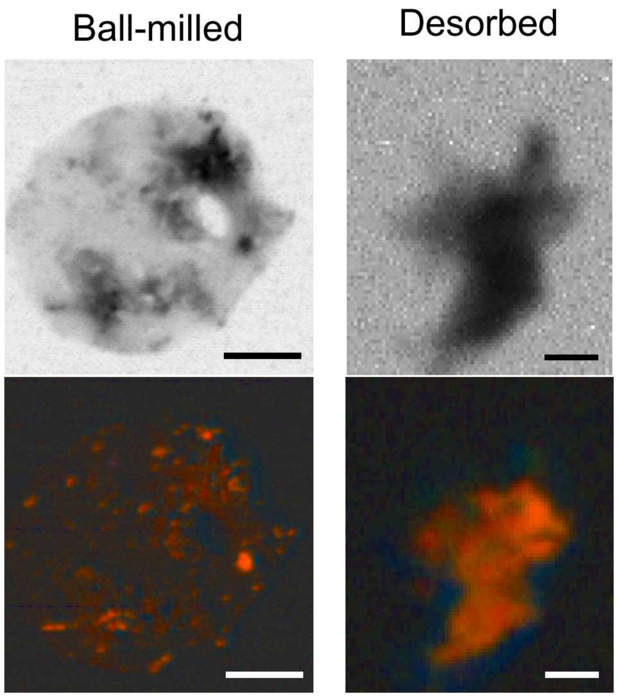
XAS shows high purity, but XPS shows significant oxidation present before milling

Titanium Localization

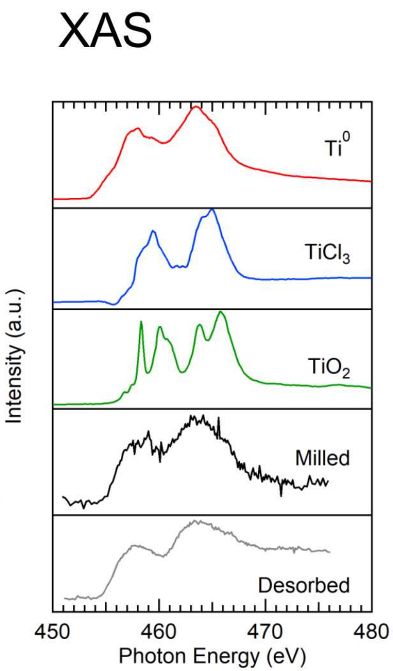
10 mol% $TiCl_3$-doped $NaAlH_4$



STXM



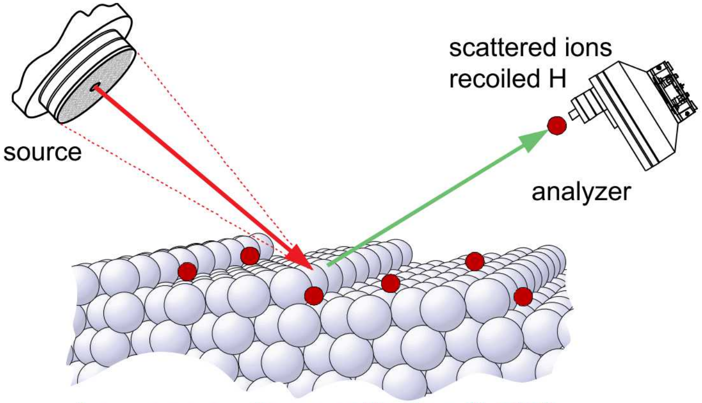
scale bars = 500 nm



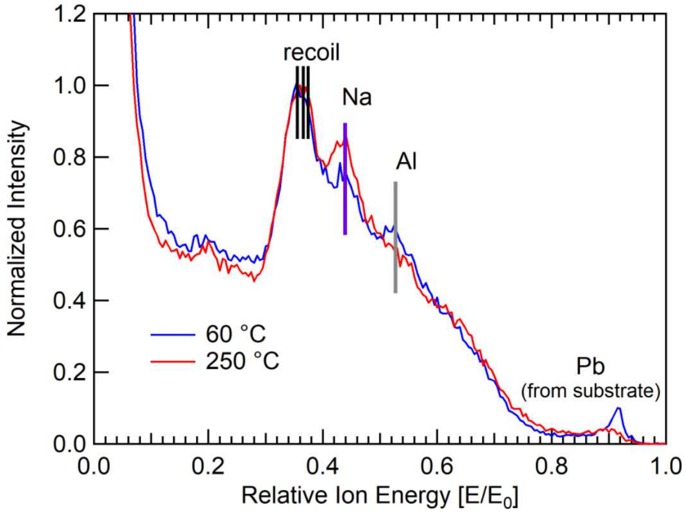
Ti not on surface until H_2 is desorbed

STXM shows Ti as predominantly metallic, not as $TiCl_3$

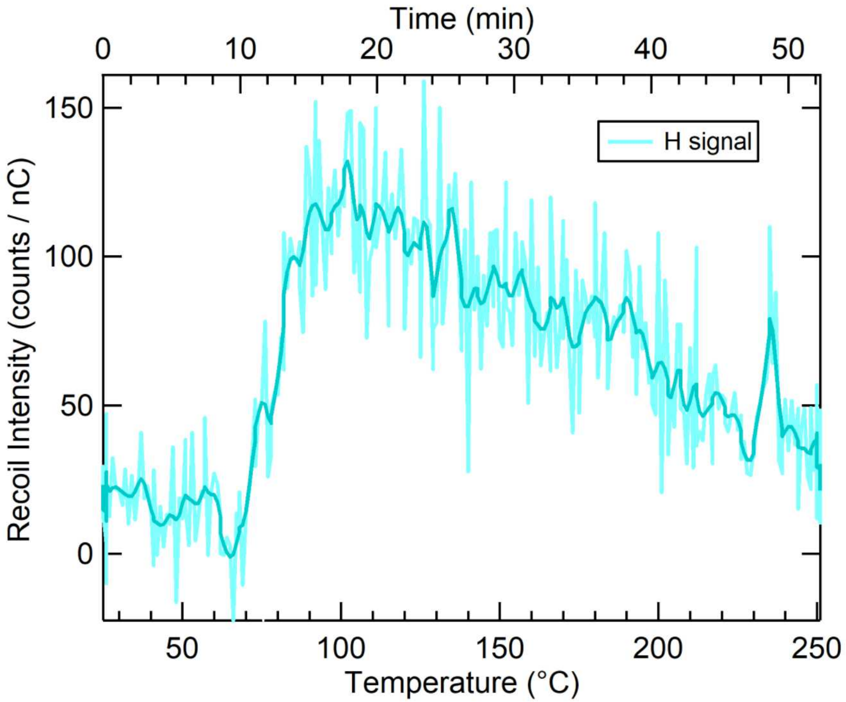
In Situ Low Energy Ion Scattering



Low energy ion scattering (LEIS):
Determine surface composition, H surface conc.
(First monolayer only, <1 nm)



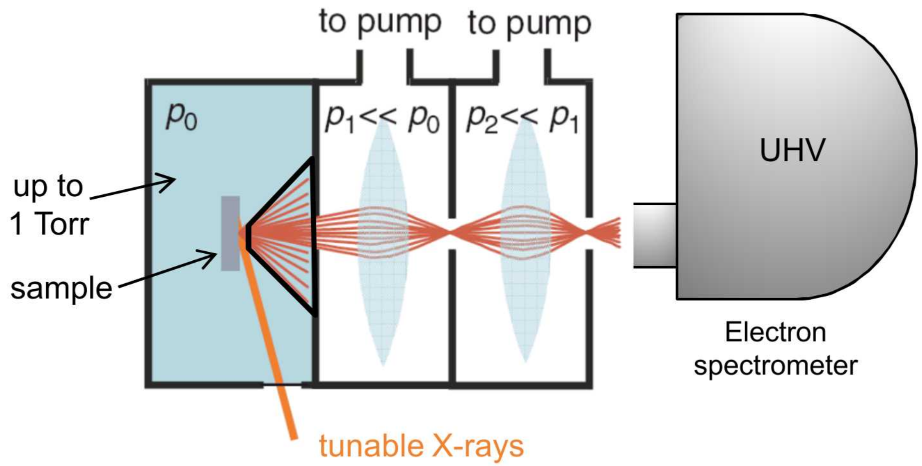
Detection not only of heavy atoms but also of surface hydrogen atoms through direct recoil



- Surface enrichment with Na after brief heating
- H starts migration to surface at ~80 °C
- Still no Ti detected

Operando AP-XPS: Monitor Chemical Changes

Ti-doped $NaAlH_4$ mounted in clean transfer case



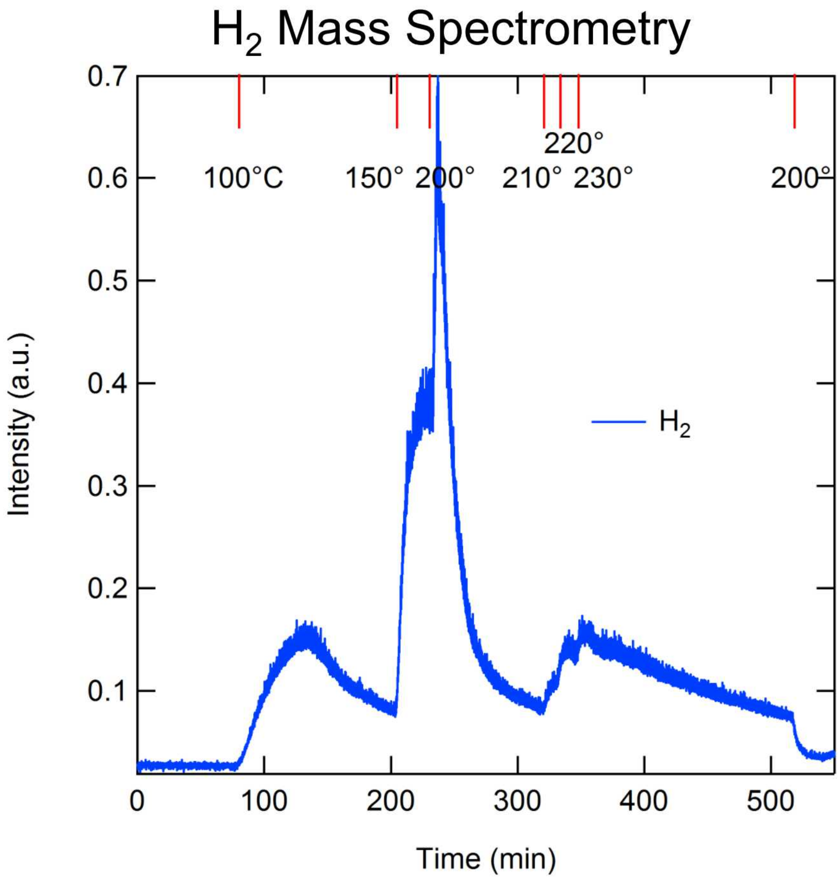
Differentially pumped chambers allow non-UHV conditions, such as sample out-gassing

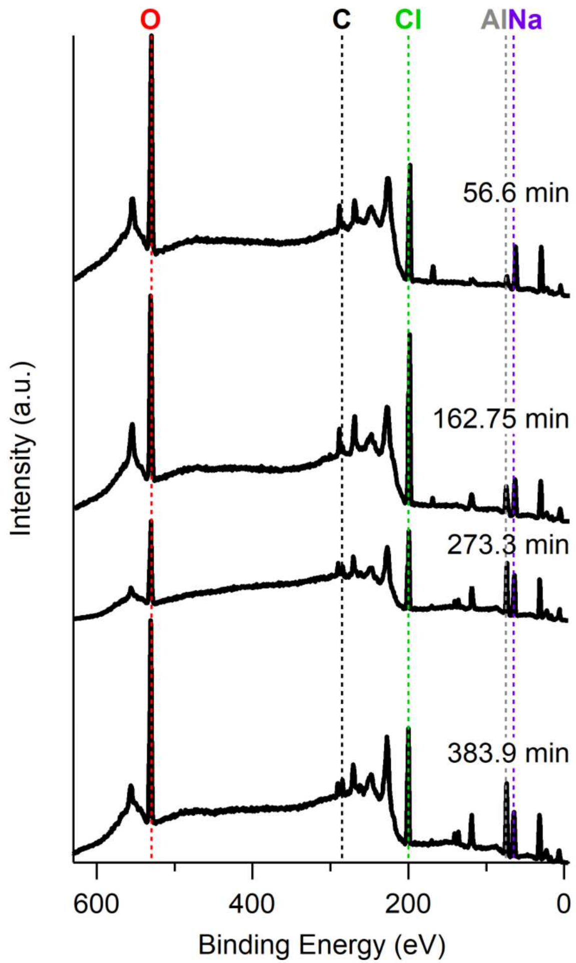
Tunable X-rays yield varying penetration depths (1-5 nm)

ADVANCED LIGHT SOURCE

Photoelectron energies reveal elements and chemical states

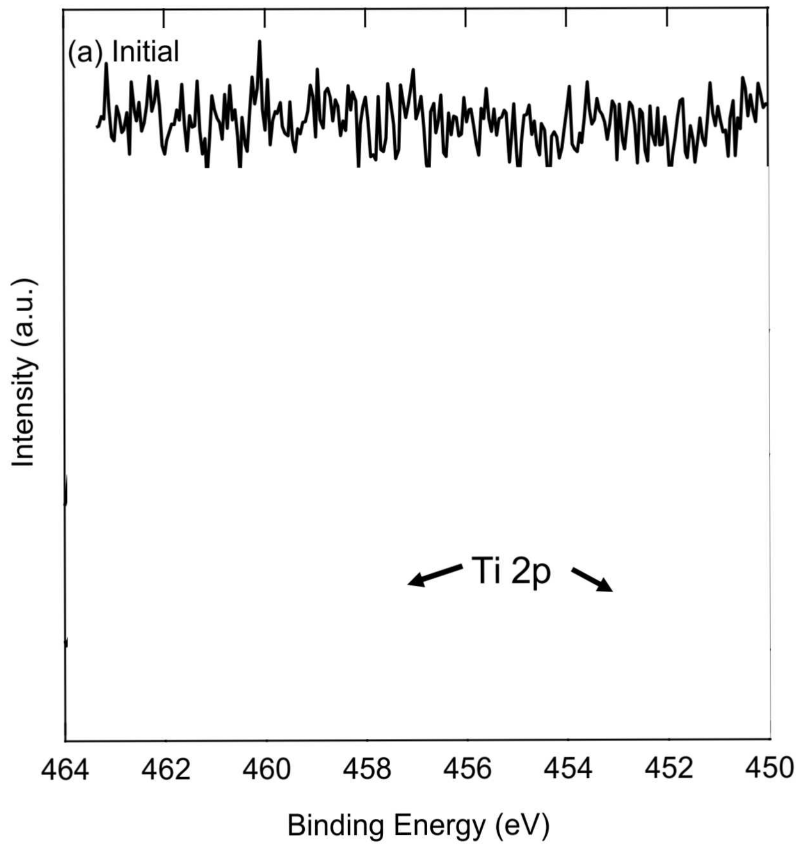
Evolution of Desorbing Hydride





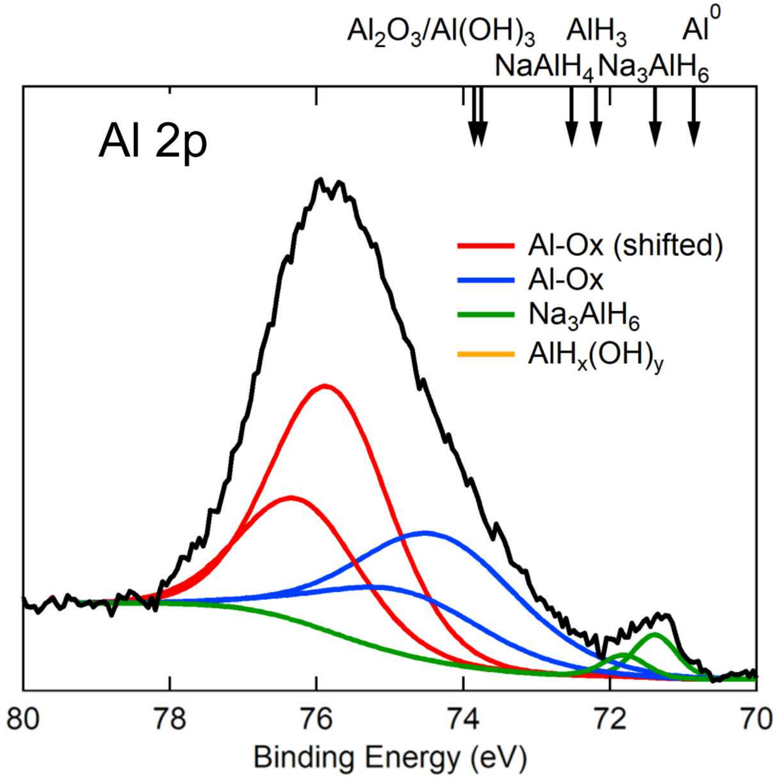
Survey spectra show substantial oxygen, even after recrystallization and clean transfer

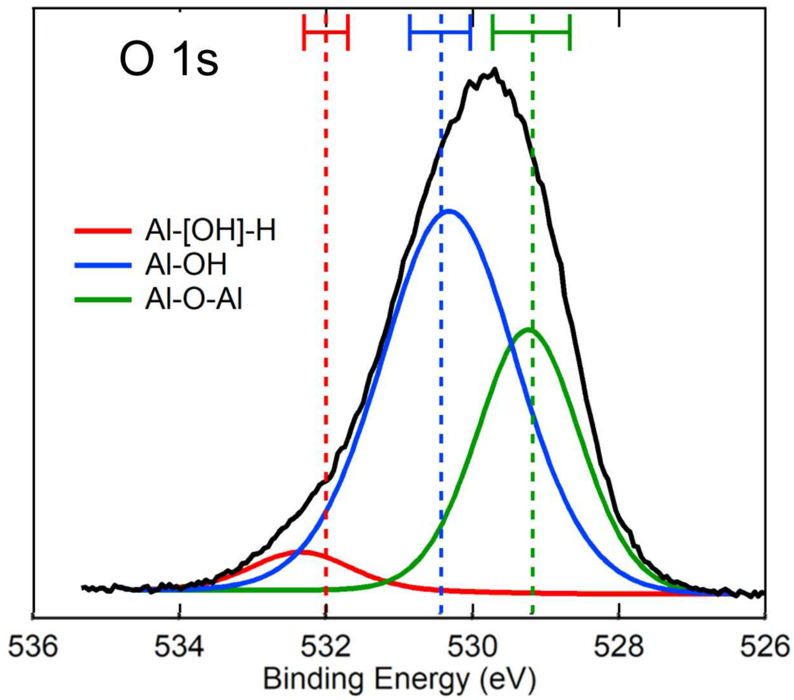
Titanium Over Time



Ti appears at surface only after extended heating

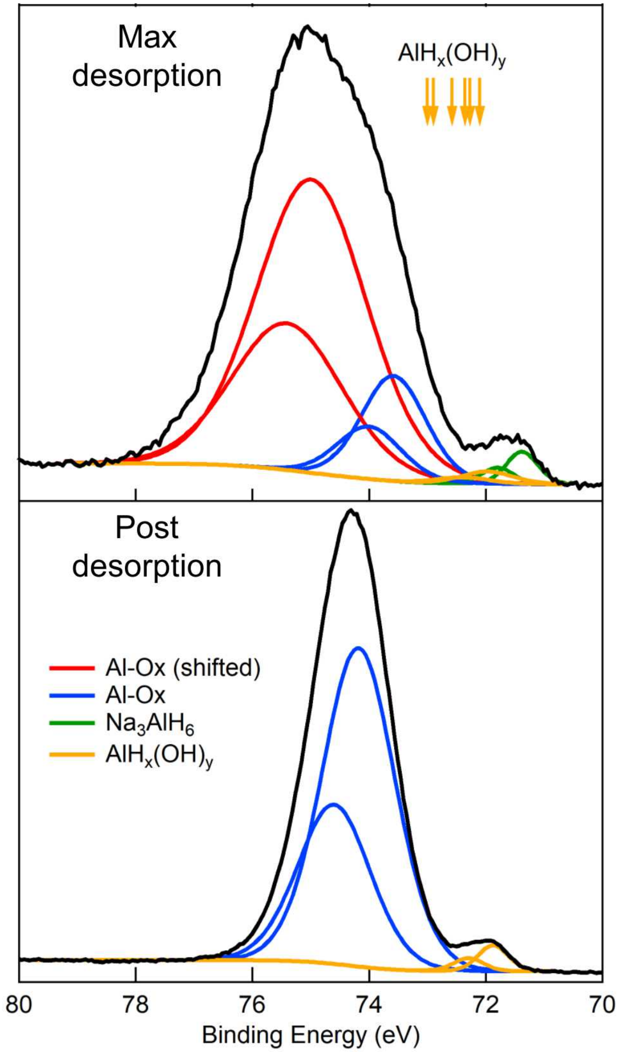
Initial Al and O Species

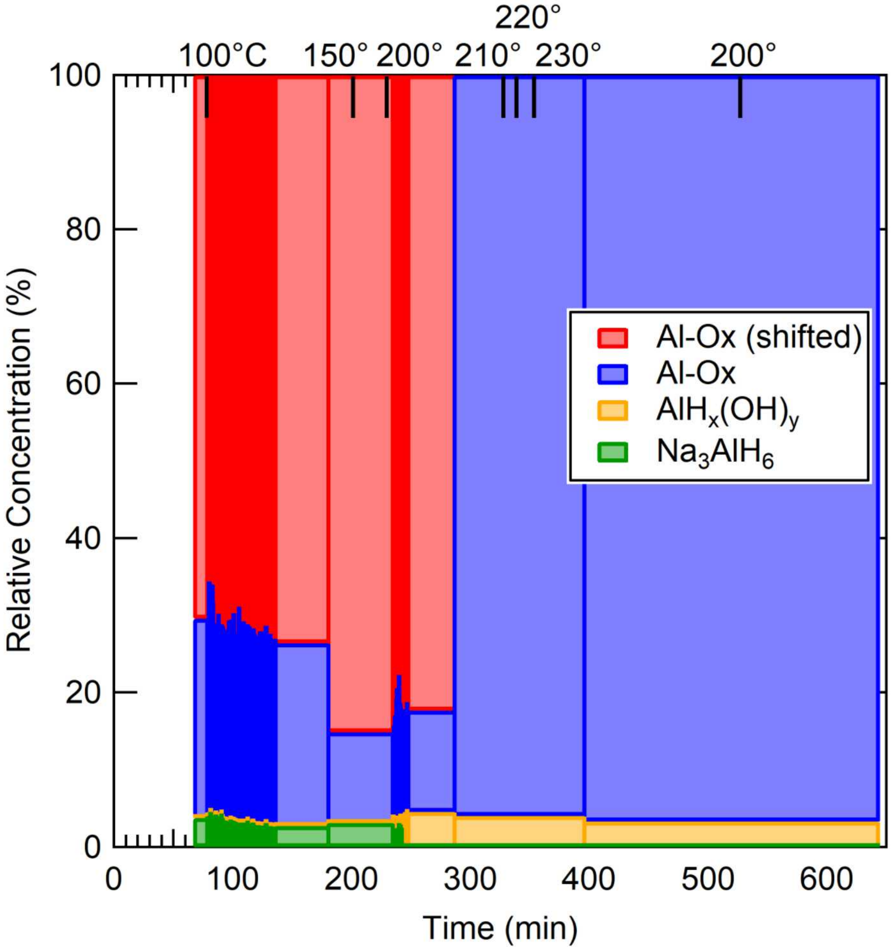




Simulated spectra inform peak assignments

Aluminum Speciation

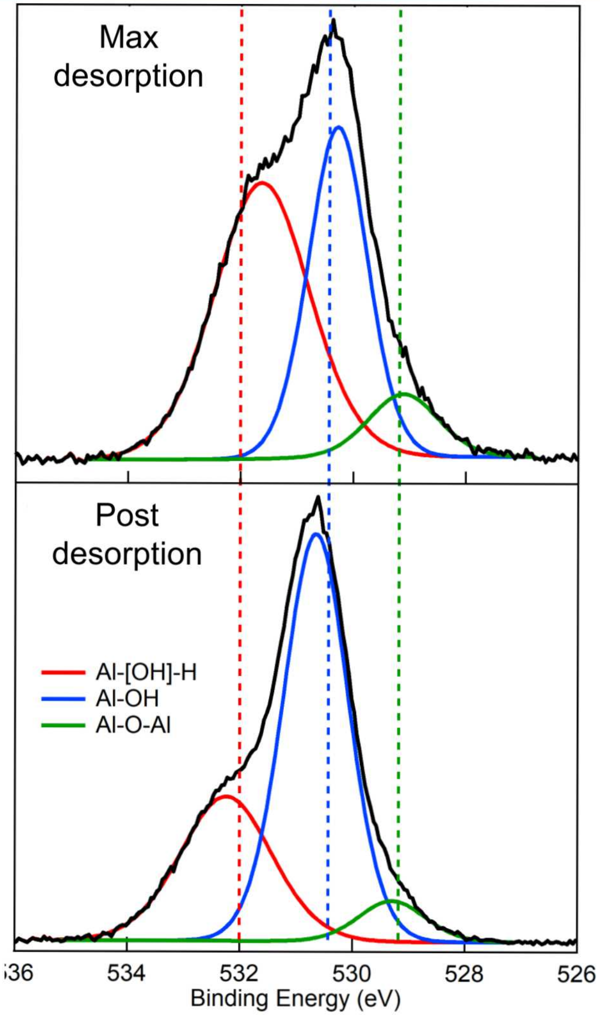


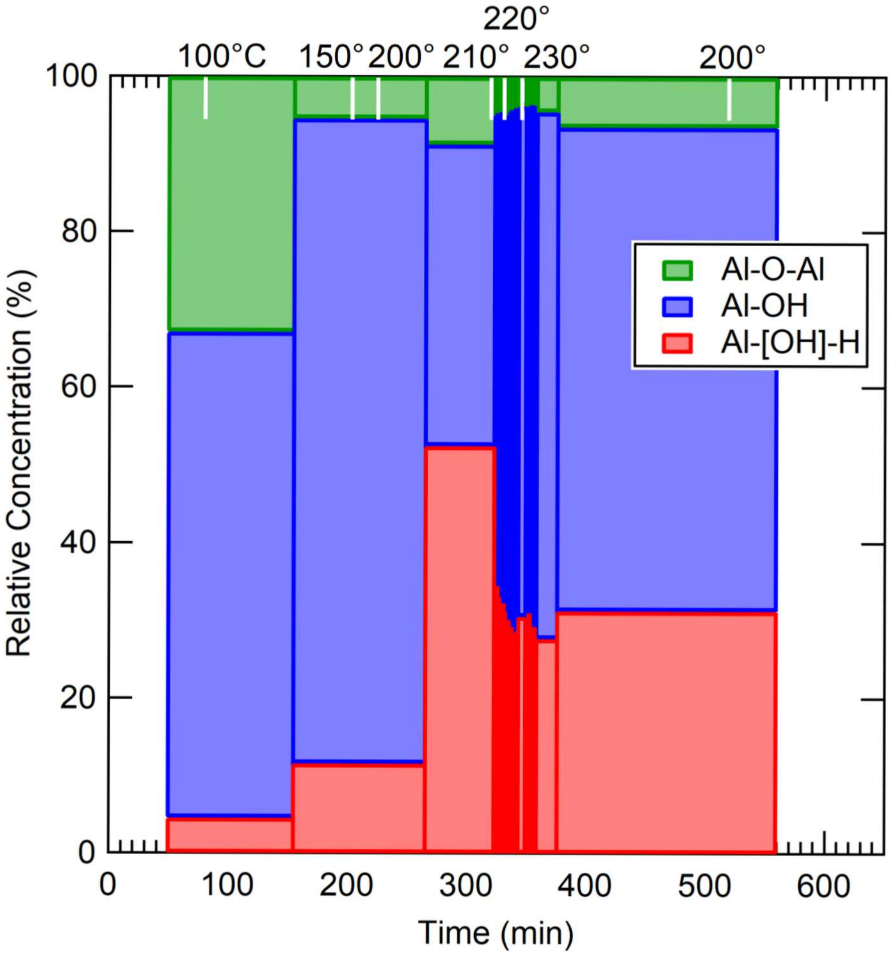


Total Al-Ox remains constant

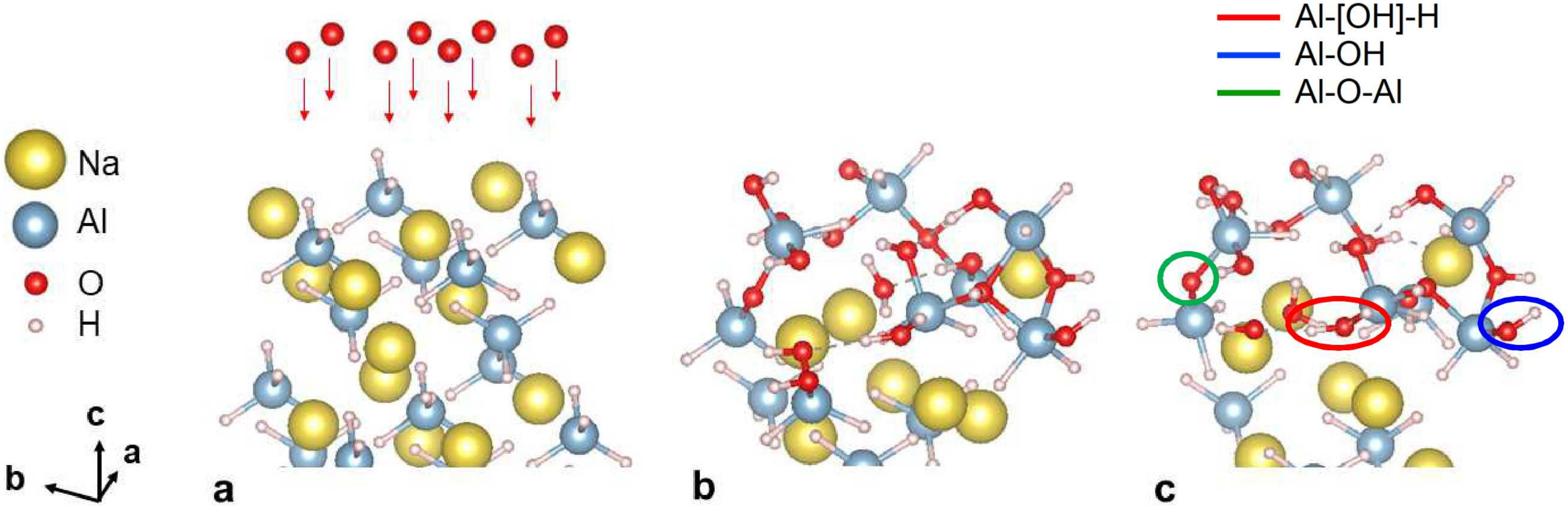
Desorbed species appears in place of Na_3AlH_6

Oxygen Becomes H-Enriched





Molecular Dynamics (MD) Simulations



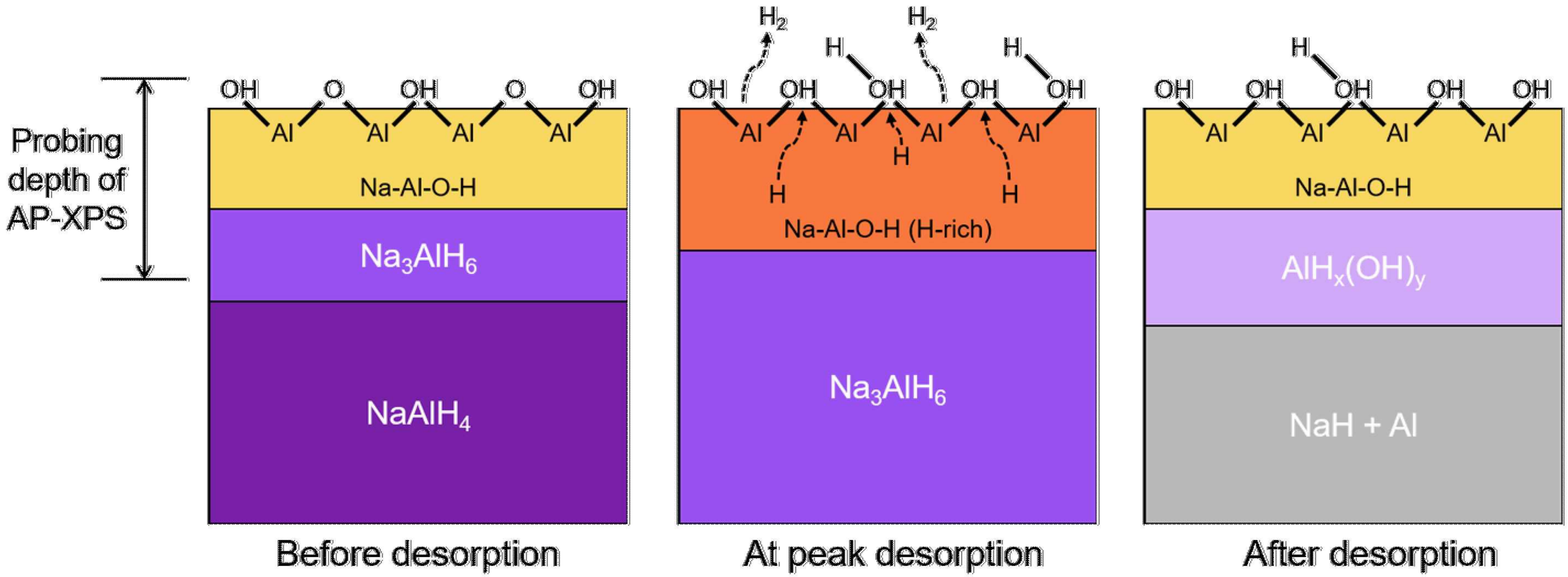
Add O atoms to $NaAlH_4$ crystal

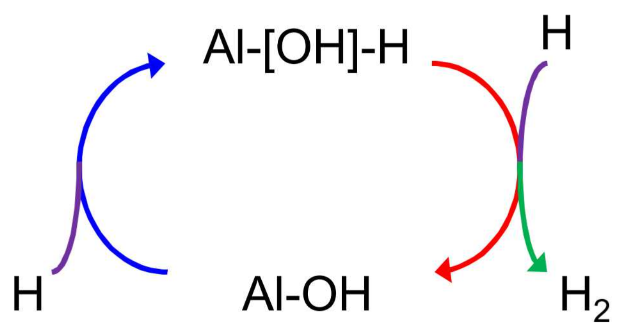
Relax structure with VASP

MD perturbation at 500 K

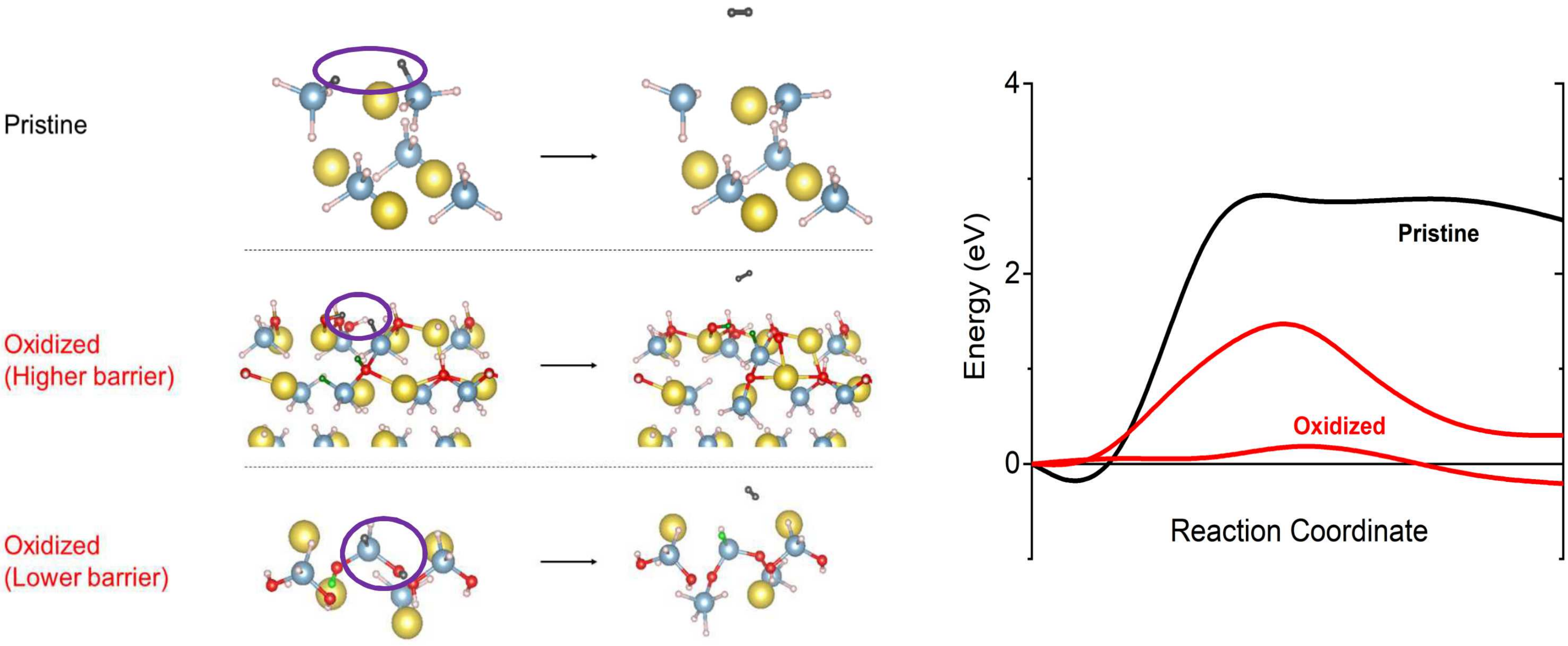
Ab initio MD shows stability and dynamicity of O-containing species on hydride surface

Proposed Mechanism of Desorption





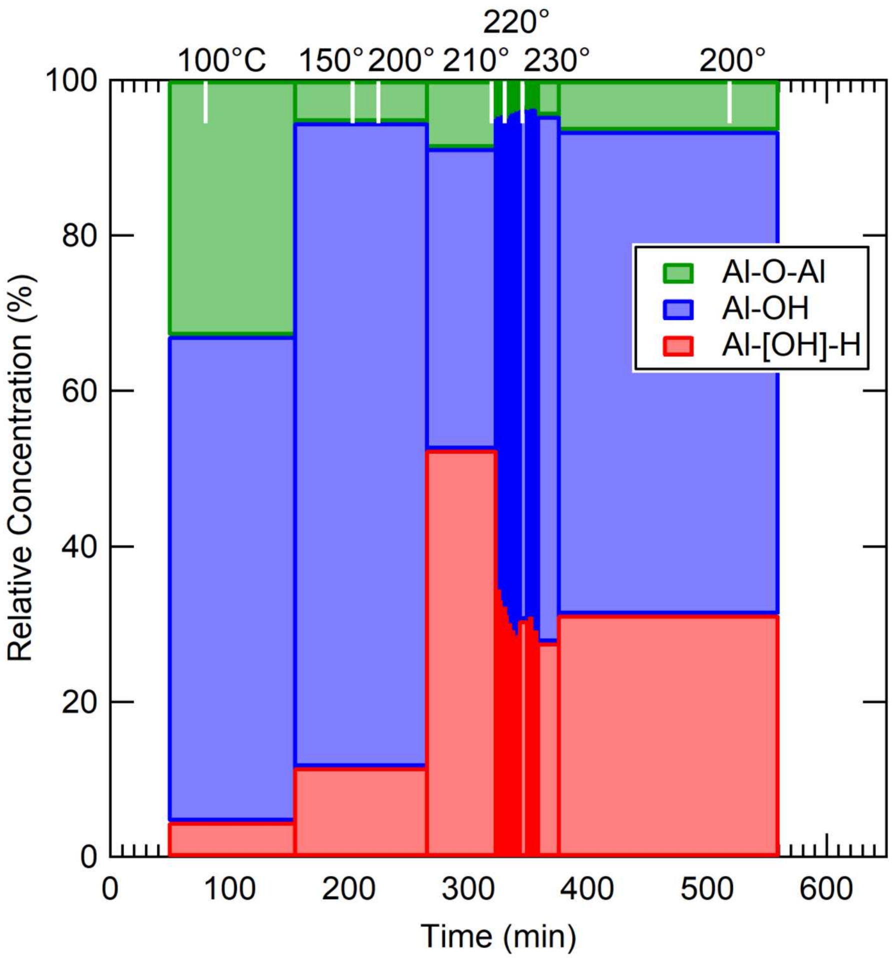
Desorption Activation Energies



Nudged Elastic Band (NEB) method: desorption easier from partially oxidized surface with both hydridic and protic H

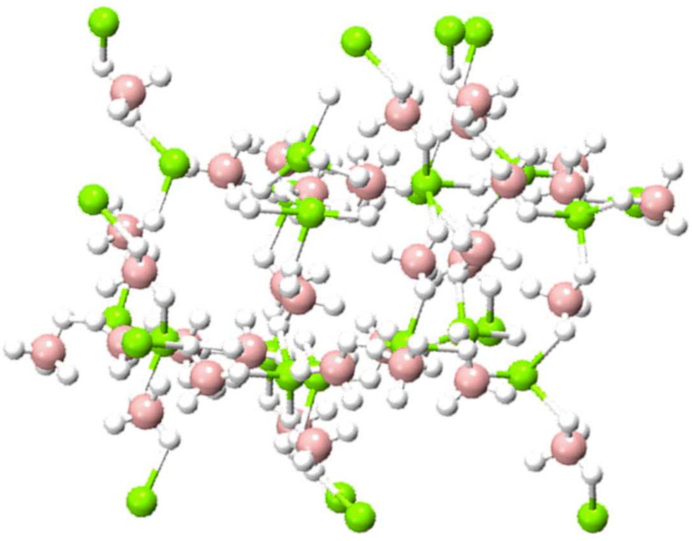
Ti-Doped $NaAlH_4$ Surface Chemistry

- Ti absent from surface until after desorption
- Surface O changes substantially in process
- Lower barriers to H_2 release with O on surface
- Ti activity must be subsurface: H transport?
- Rehydrogenation roles at surface unknown and hard to probe

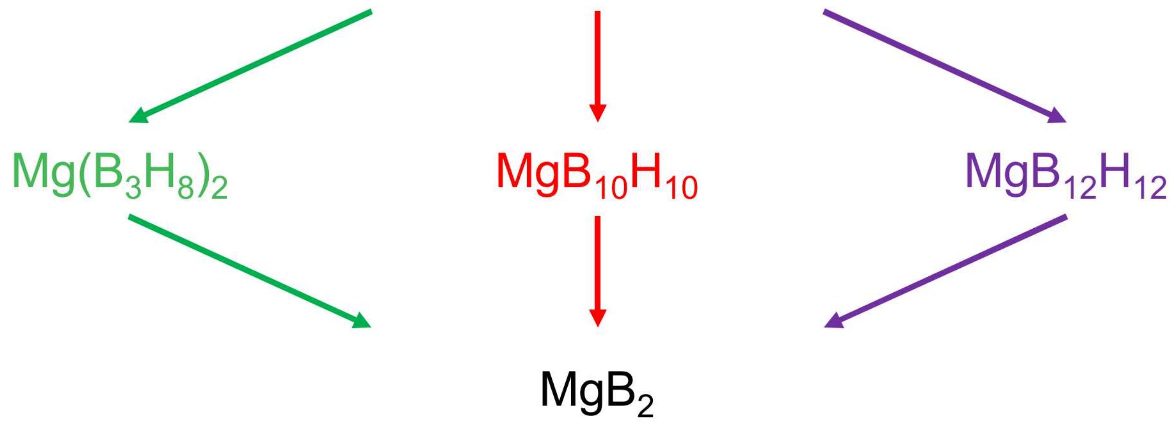


Applicability to Other Hydrides?

- Surface oxidation likely widespread occurrence in air- and moisture-sensitive hydrides
- $NaAlH_4$ not very high capacity (5.6 wt.% H usable)
- Magnesium borohydride ($Mg(BH_4)_2$) has capacity of 14.9 wt.%



$Mg(BH_4)_2$



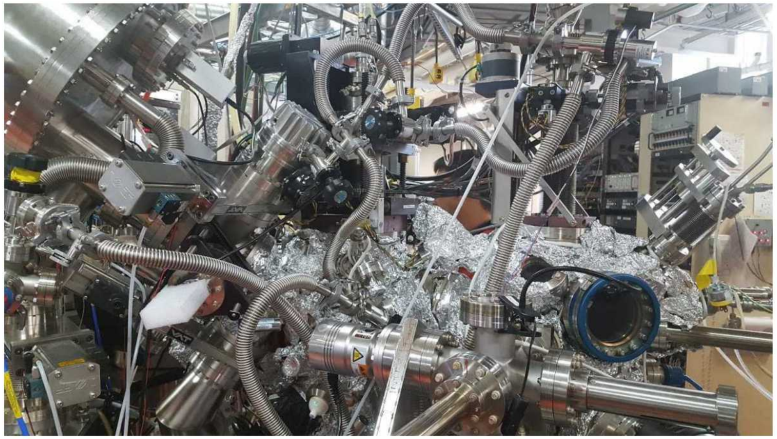
Very complex boron cluster chemistry

High temperature (~ 600 °C) needed for complete desorption

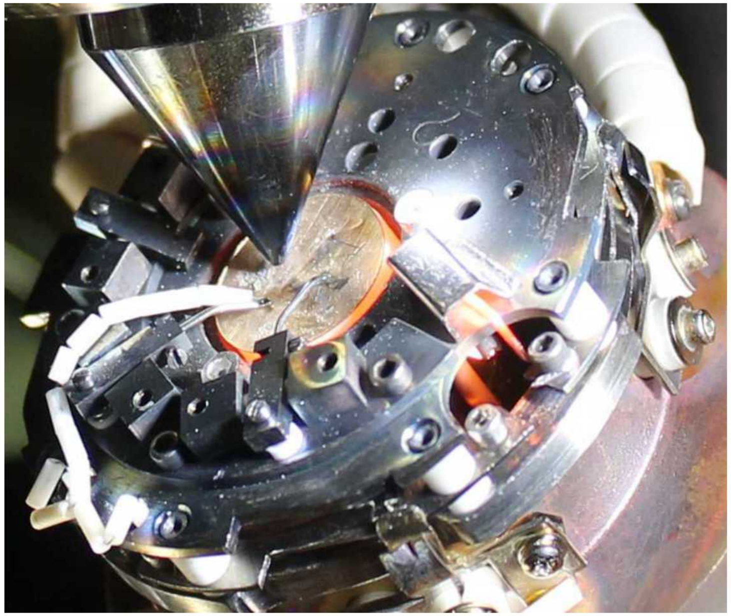
Reversibility only at high H_2 pressures (> 500 bar)

ALS AP-XPS General User Proposal

- Additional 100 h of instrument time to study hydrides *in situ*
- Collected >1500 spectra on $Mg(BH_4)_2$ desorbed up to 600° C
  - Included $Mg(BH_4)_2$ samples after exposures to O_2, H_2O, and air
  - Data analysis still ongoing

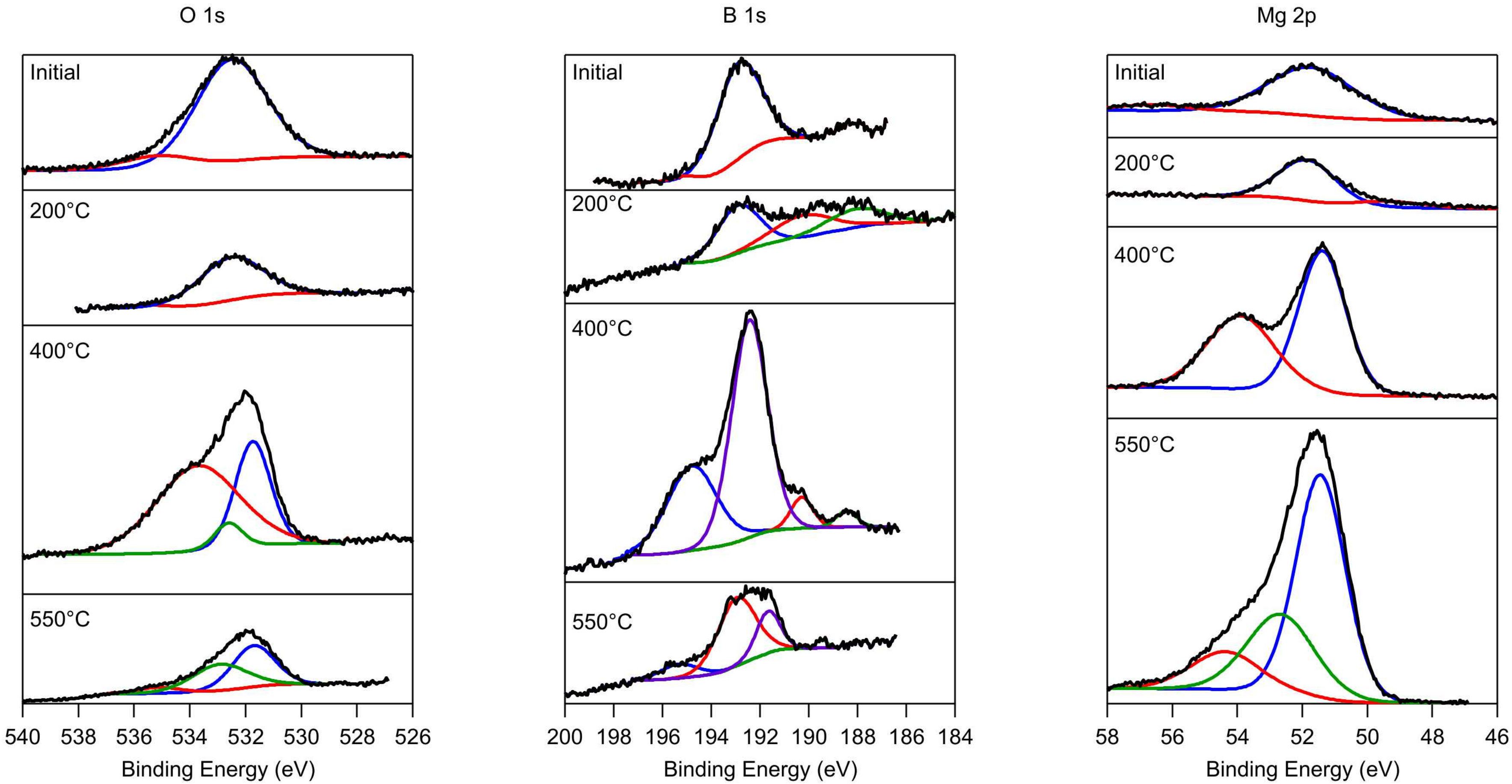


AP-XPS at BL11.0.2



$Mg(BH_4)_2$ on Au foil at 600 °C

Preliminary AP-XPS Results



B-O species shift to more B-OH character above desorption temperature (~200 °C)

B starts oxidized; numerous new species appear after heating

Mg segregates to the surface at high temperatures in different chemical environments

Conclusions

- Highly dynamic dehydrogenation of $NaAlH_4$ was observed
- Oxidic species play substantial role in desorption mechanism
- Titanium not near surface during H_2 loss
- Cleanliness difficult to achieve
- Combination of theory and *in situ* experiments enable comprehension of behaviors during dehydrogenation
- Other hydrides (e.g., $Mg(BH_4)_2$) currently under investigation

HyMARC Collaboration and Funding Partners

Sandia National Laboratories

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Mark Allendorf

Lawrence Livermore National Laboratory

Andrew Rowberg
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