SAND2017-10760C

Promotion of Dehydrogenation of Ti-Doped NaAlH4 by Dynamic Surface Hydroxides Measured *in operando*

October 4, 2017

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

Hydrogen Storage

- 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

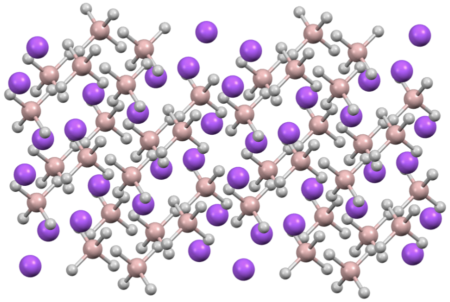
Compress

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

Liquefy

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

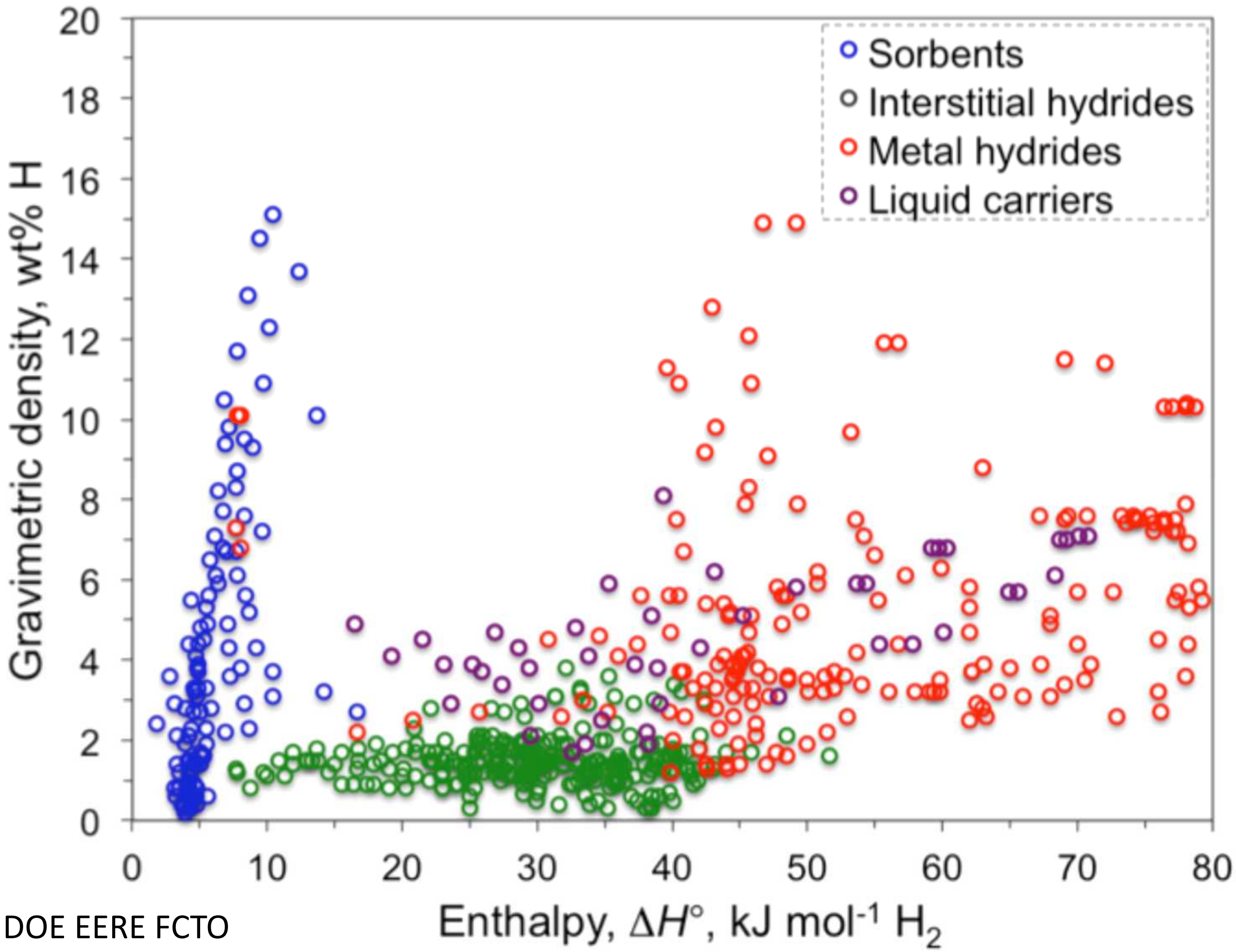
Solidify



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

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

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. ($\Delta H \approx$20-30 kJ/mol H_2)
  - Reversible (1500 cycles)
  - 1.5 kg H_2 / min fill rate

Need “Goldilocks” thermochemical properties and fast kinetics!

Metal Hydrides-Issues and Questions

Hydride	Theoretical wt% H
PdH	0.9
$NaAlH_4$	7.4
MgH_2	7.5
$LiNH_2$ + 2 LiH	10.3
$Mg(BH_4)_2$	14.8

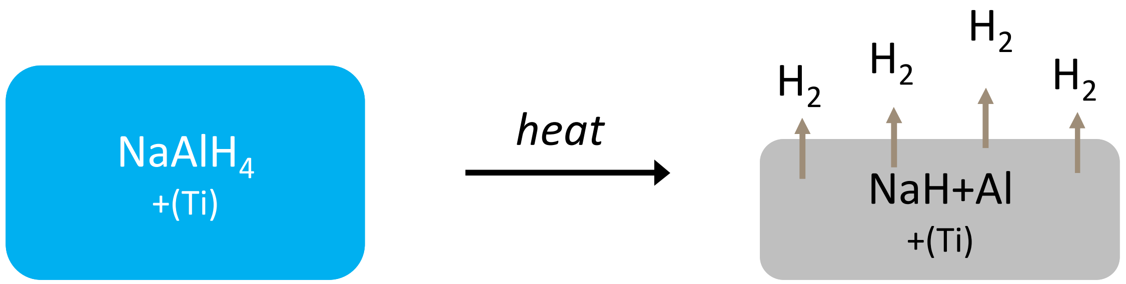
- High capacity targets
- Complex reaction pathways
- Formation of intermediate(s)
- Understanding mechanism and role of catalysts

➡ Ti-doped $NaAlH_4$ as model system

Ti-Doped $NaAlH_4$

$$3\ NaAlH_4 \rightleftharpoons Na_3AlH_6 + 2\ Al + 3\ H_2$$
$$Na_3AlH_6 \rightleftharpoons 3\ NaH + Al + {}^{3}/_{2}\ H_2$$

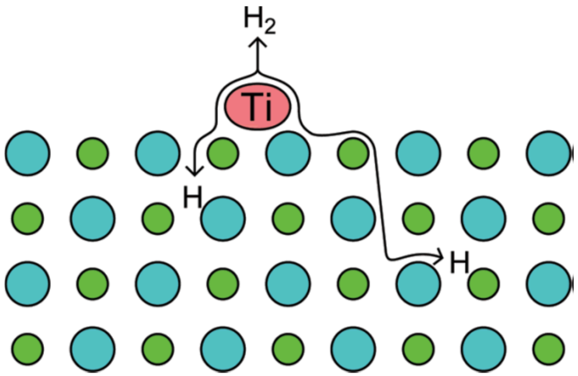
$+\ TiCl_3$



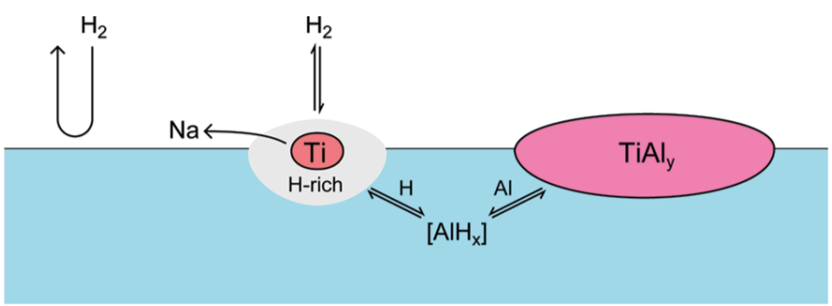
What **form** of Ti is present and what is its **role** in (de)hydrogenation at the surface?

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

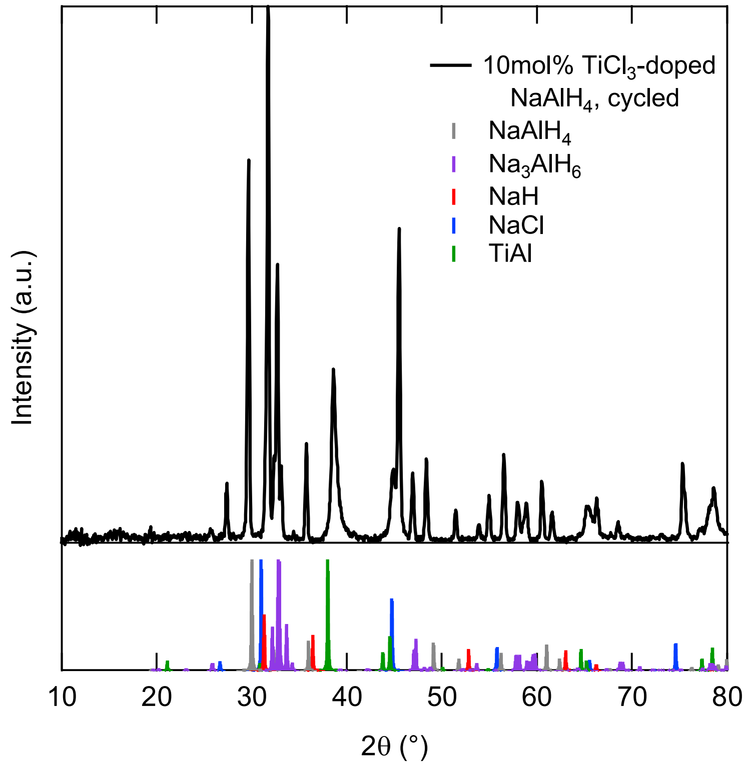


Ti alloys with Al and encourages Na vacancies while bringing H atoms together

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

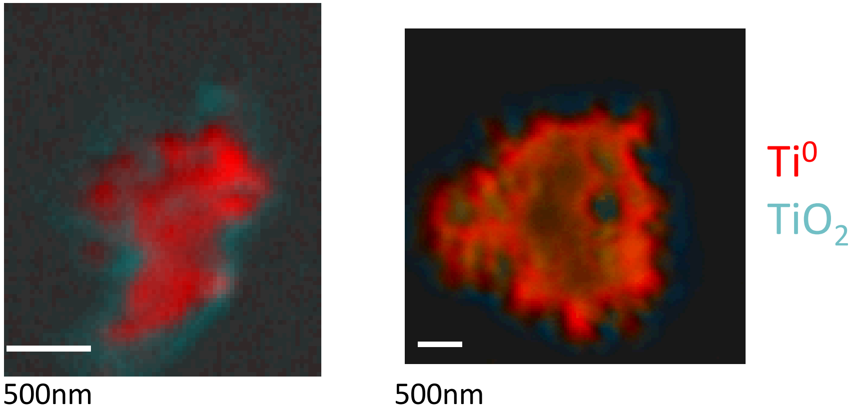
Bulk Characterization

Recryst. $NaAlH_4$ ball-milled with 10 mol% $TiCl_3$ for 2 hours
Resulting powder cycled (dehydrided and rehydrided) 5 times



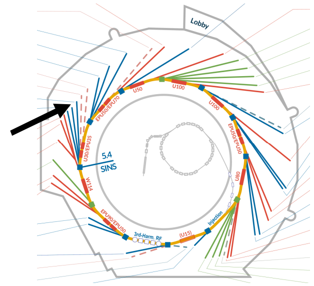
XRD shows TiAl alloy phase after cycling

Ti L edge STXM



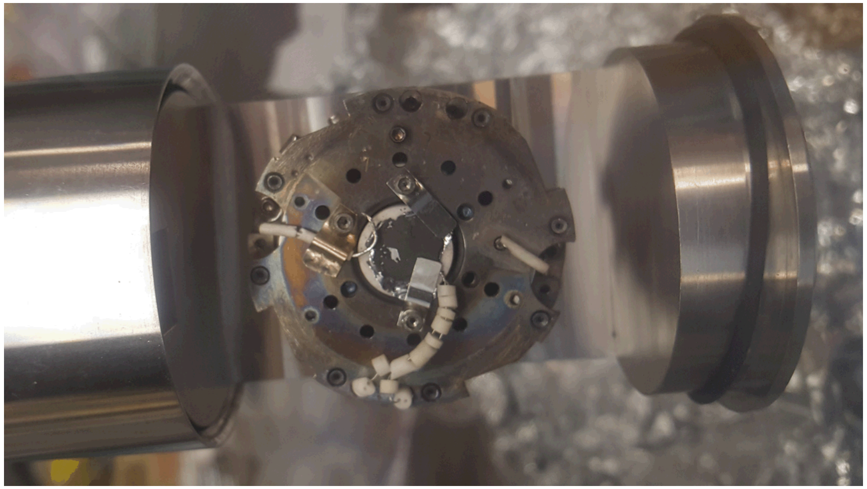
Metallic (non-oxidized) Ti present in both hydrogenated and dehydrogenated states

At BL 5.3.2.2
ALS-08049



In operando Desorption Experiments

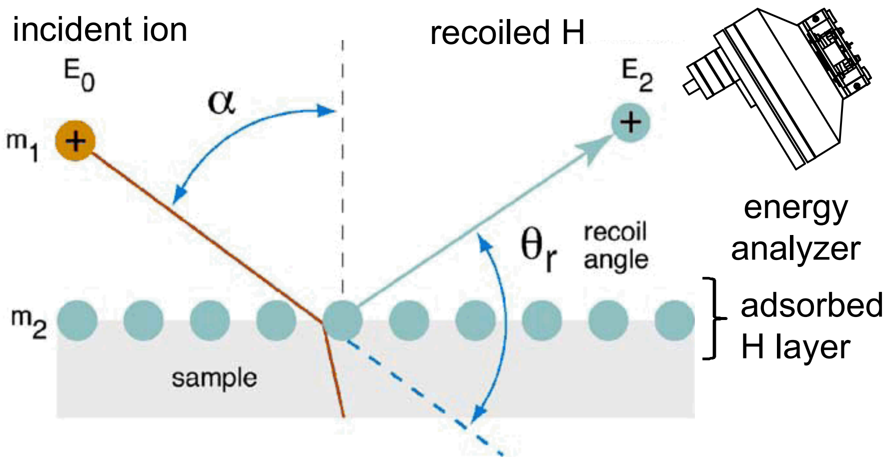
- Powder pressed into Pb-alloy foil (mp = 296 °C)
- Sample cleanly transferred to UHV chamber on holder with heater
- Initial measurements performed before heating begun

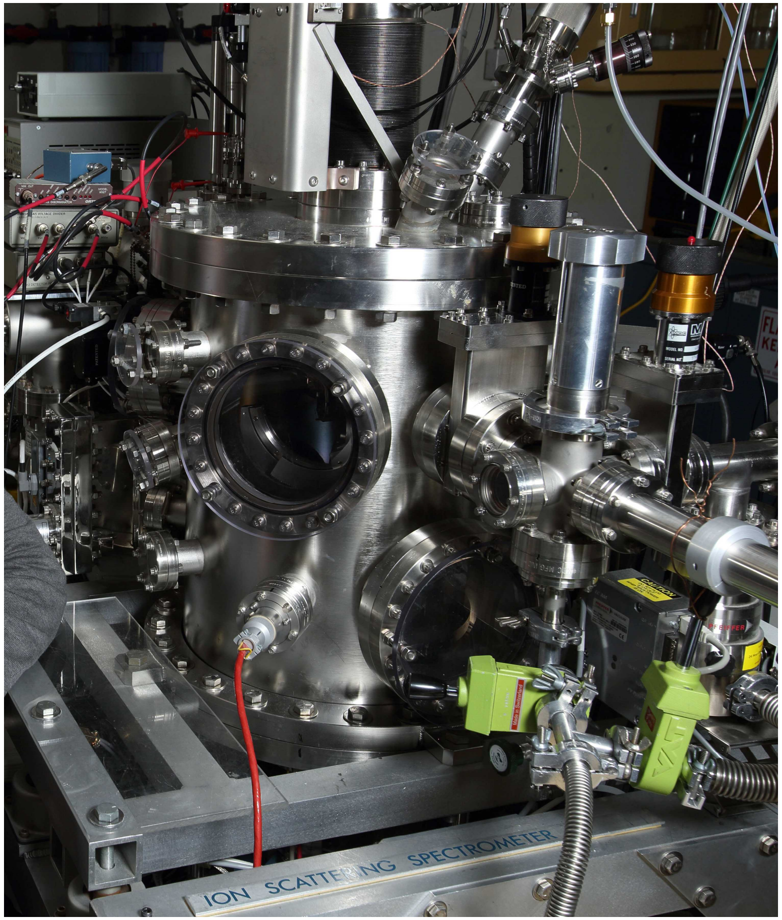


10 mol% $TiCl_3$-doped $NaAlH_4$ mounted on sample holder with heater

Low-Energy Ion Scattering (LEIS)

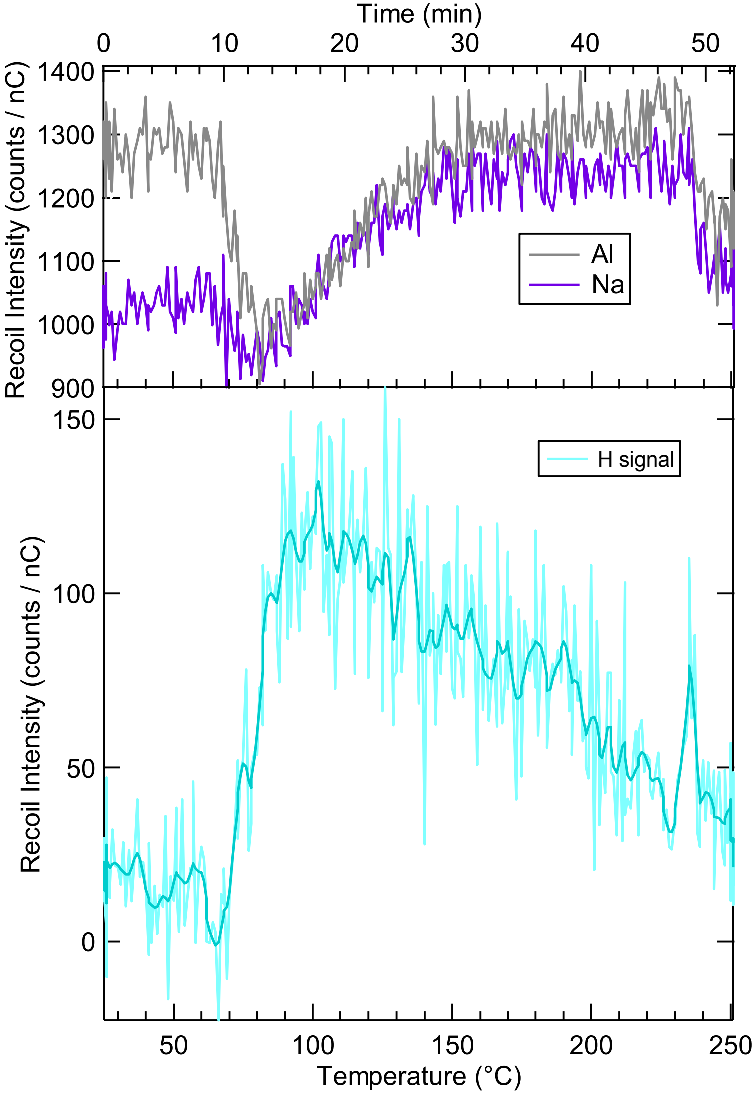
- Only technique to detect surface H directly with ion recoil spectroscopy
- Highly sensitive to first atomic layer of surface

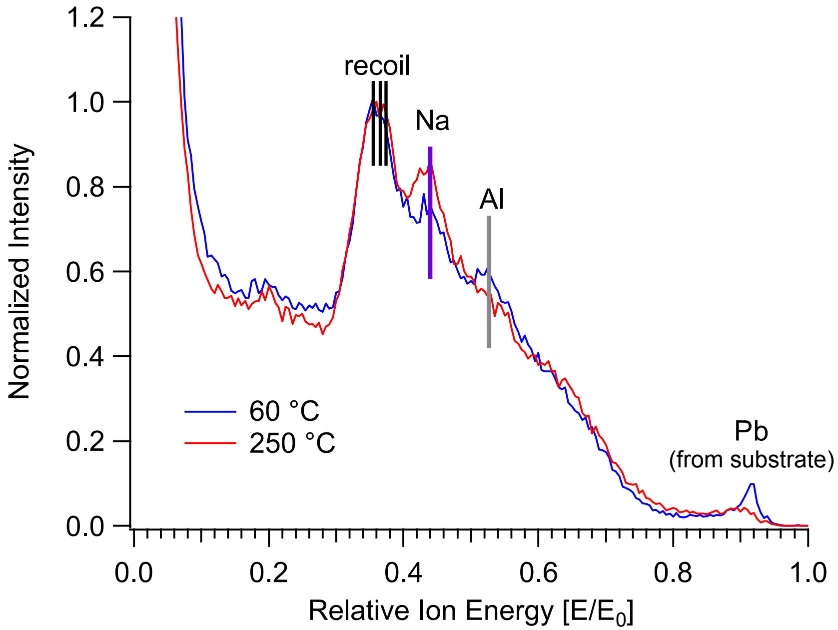




Sandia's LEIS system

LEIS Results

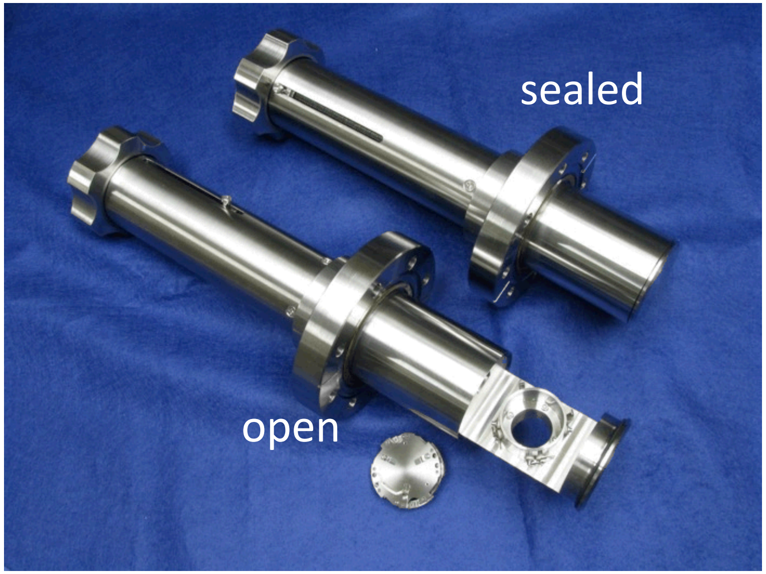




- H starts migration to surface at ~80 °C
  - Lower than desorption temperature of ~150°C
- Surface enrichment with Na after heating
- No Ti detected

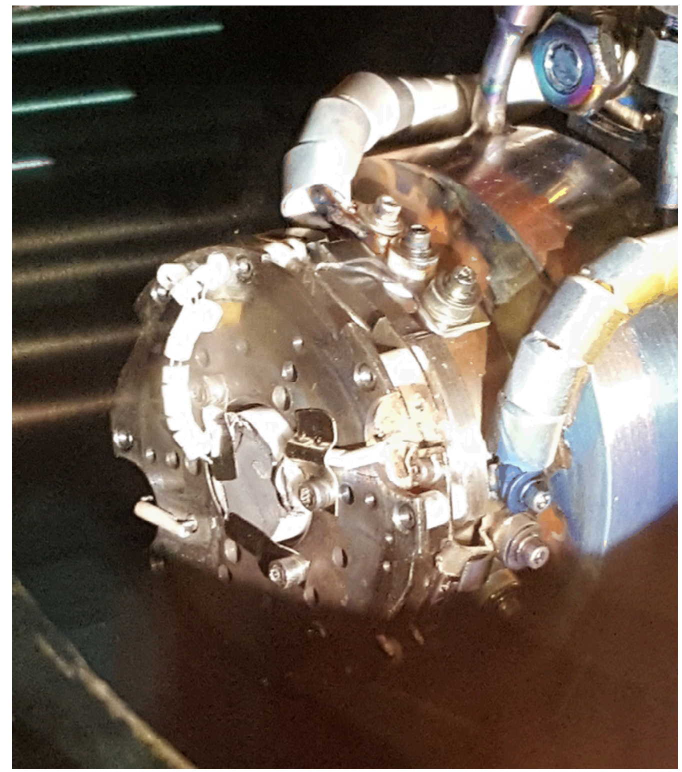
R. Kolasinski, J. Whaley

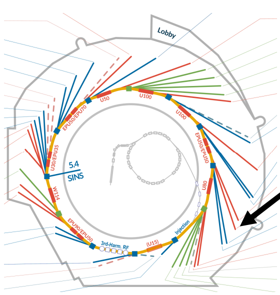
Monitoring Hydride Desorption *In Operando*



Clean transfer from glovebox to UHV

Heating on 11.0.2
APPES manipulator

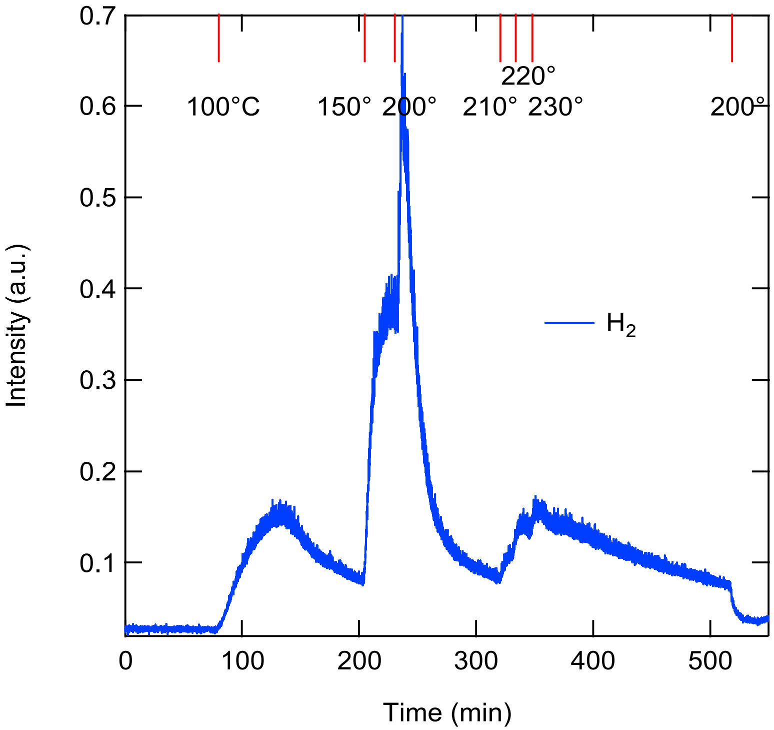




At BL 11.0.2
RAPIDD

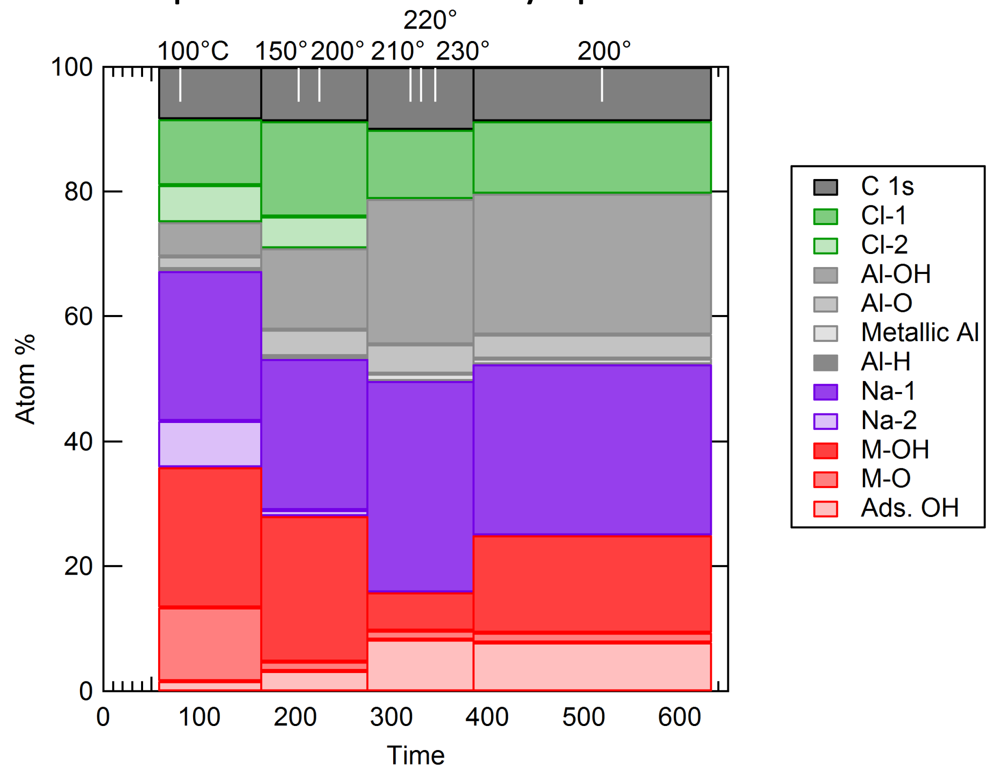
AP-XPS Shows Highly Dynamic System

Mass Spectrometry



H_2 release observed by MS

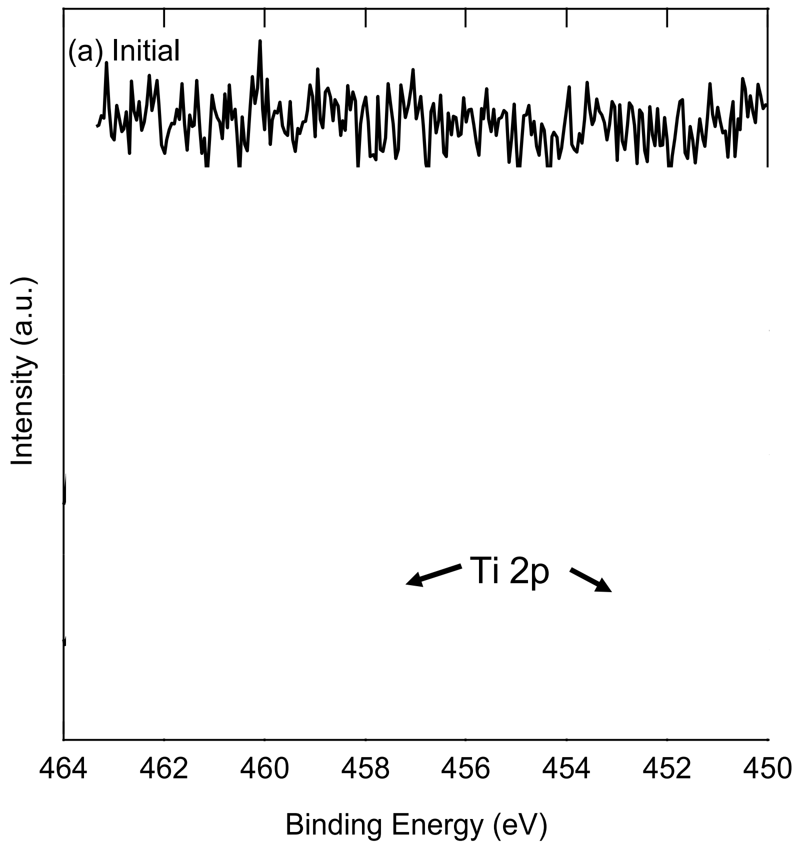
Species from Survey Spectra

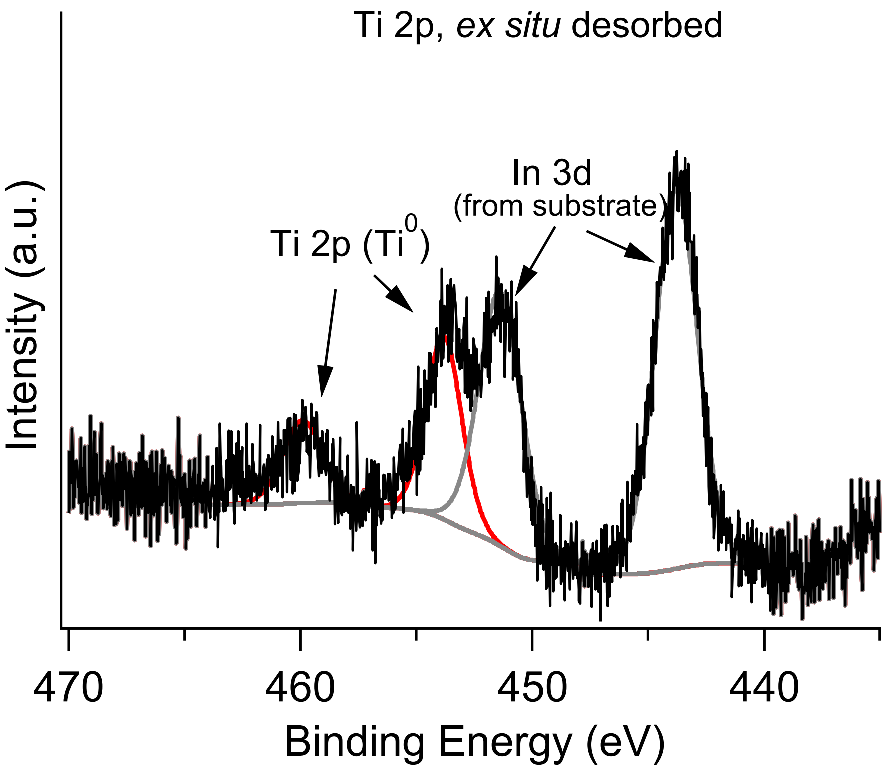


Numerous species from four different elements were present and shifted in relative abundance with heating over time

N.B.: Indicated temperatures approximate

Titanium Dopant

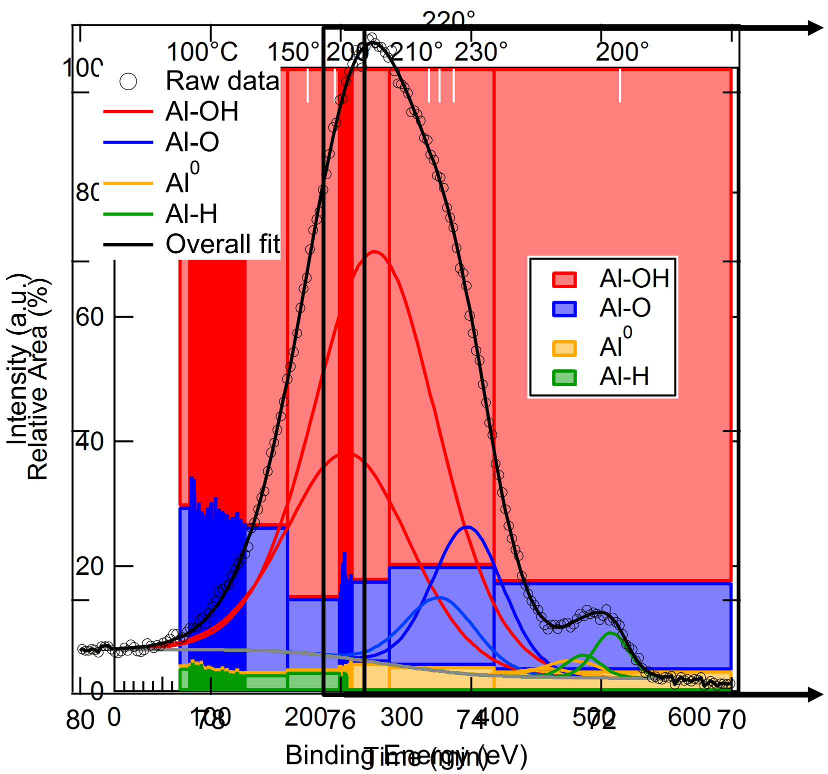


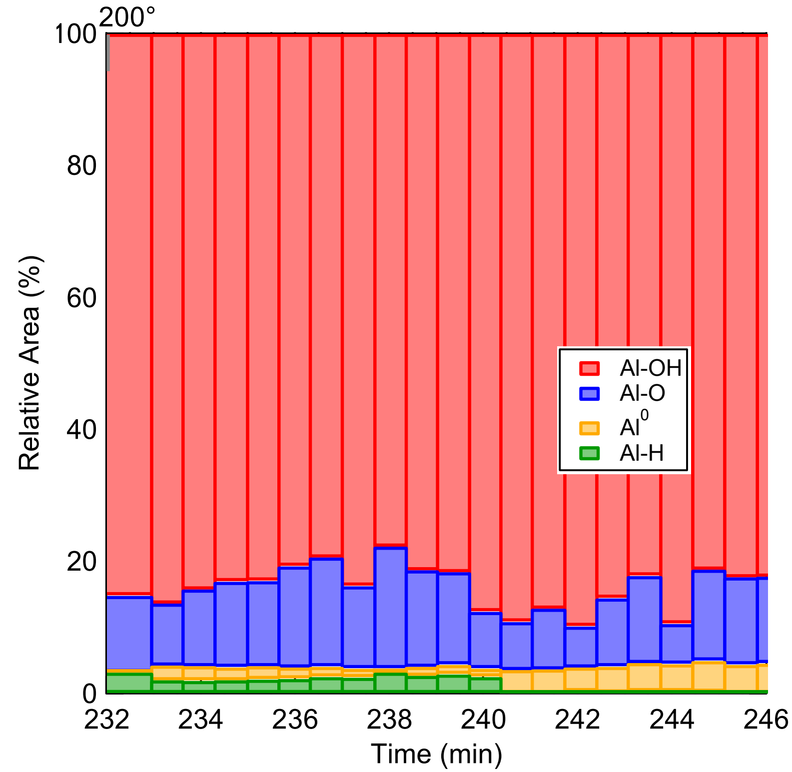


Appears after extended heating

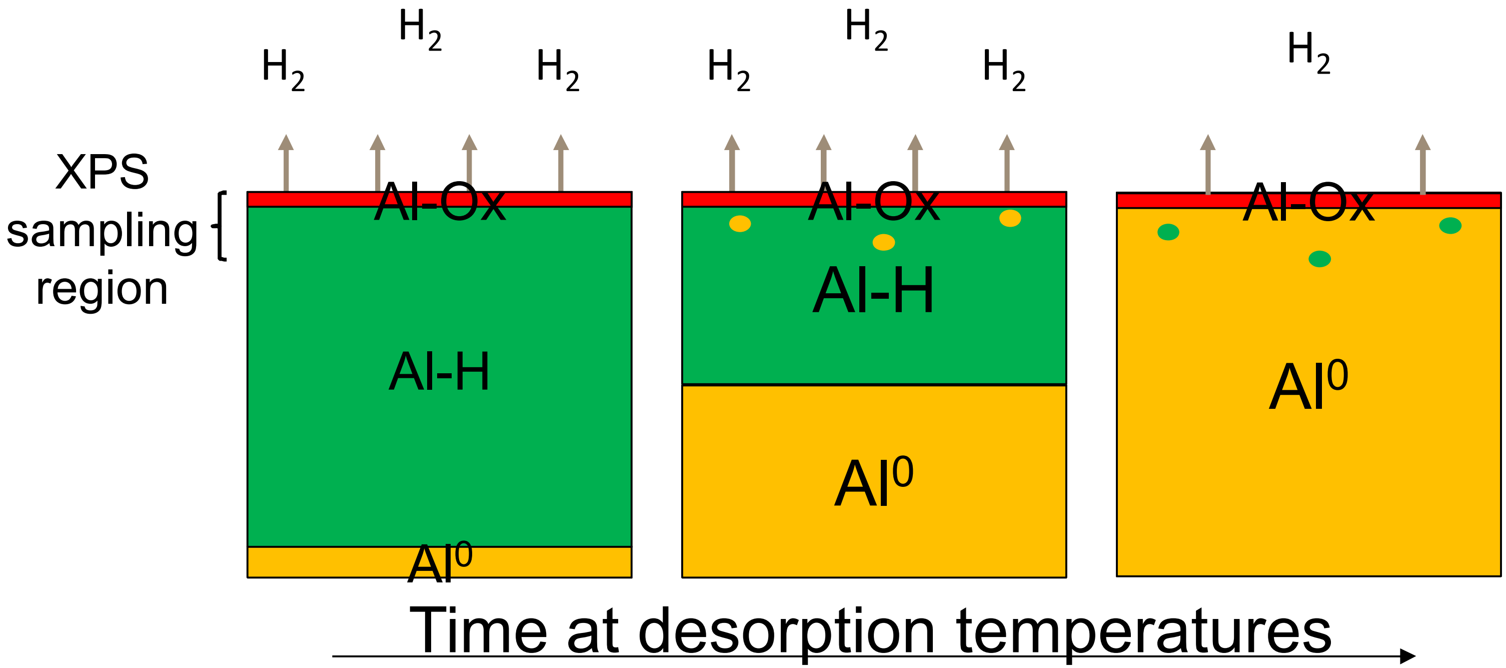
Present at surface after desorption

Al Dehydrogenation Observed

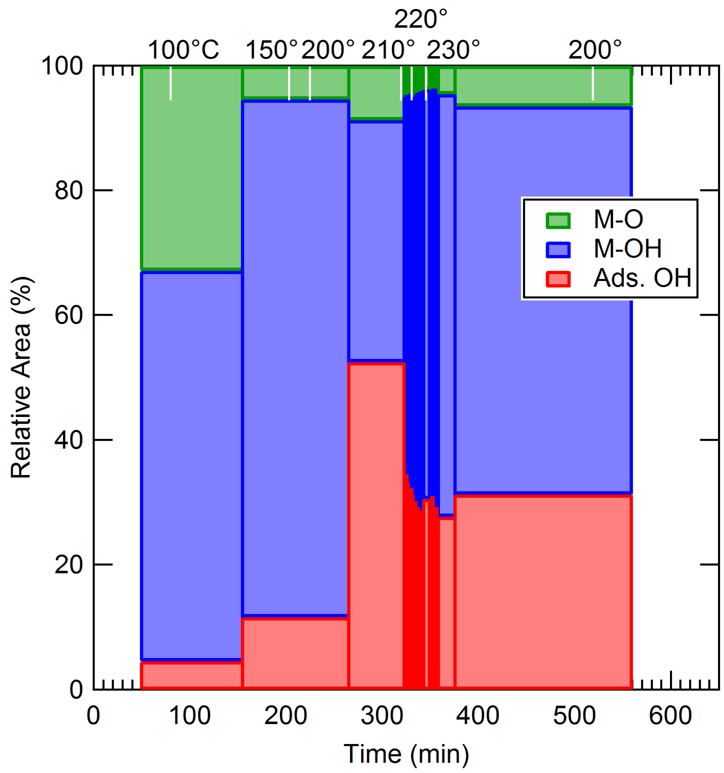


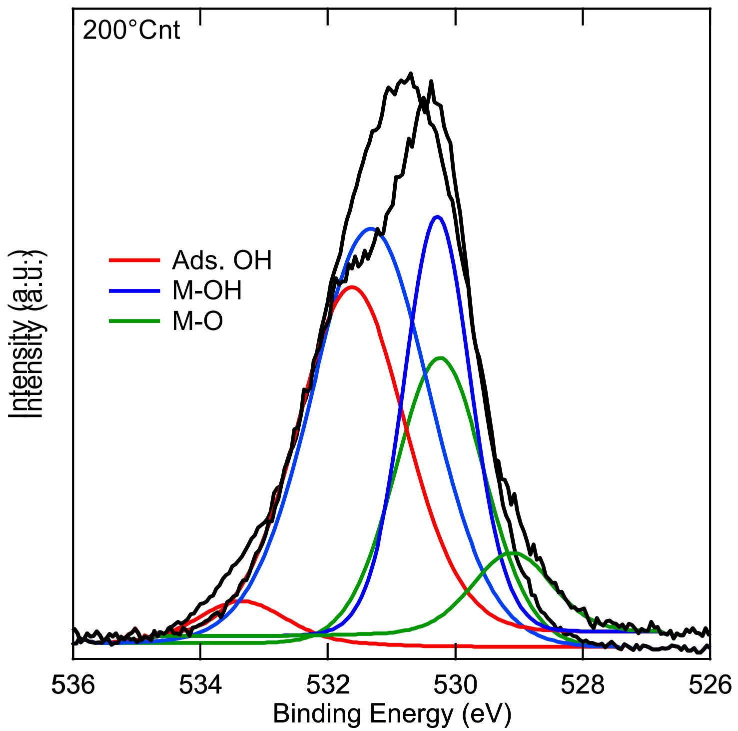


Propagation of Dehydrided Phase



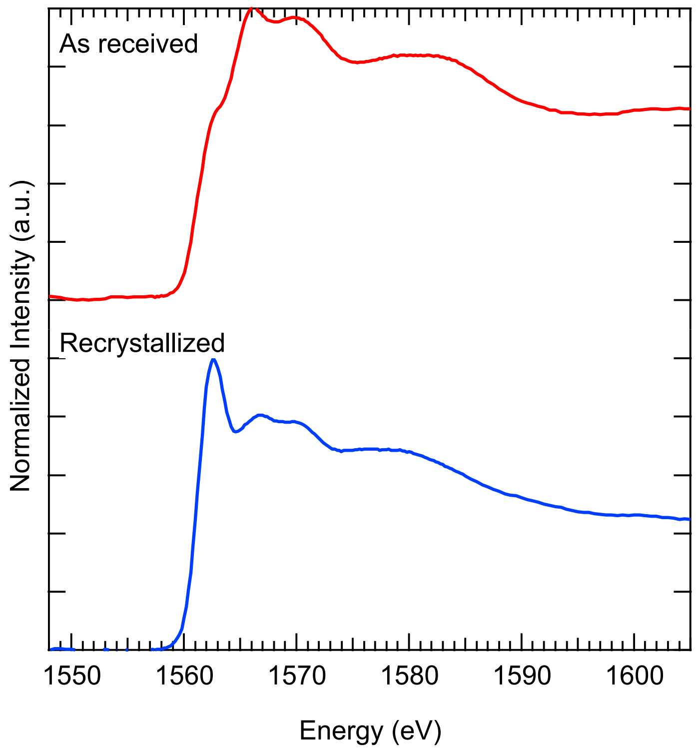
Dynamic Oxygen Species

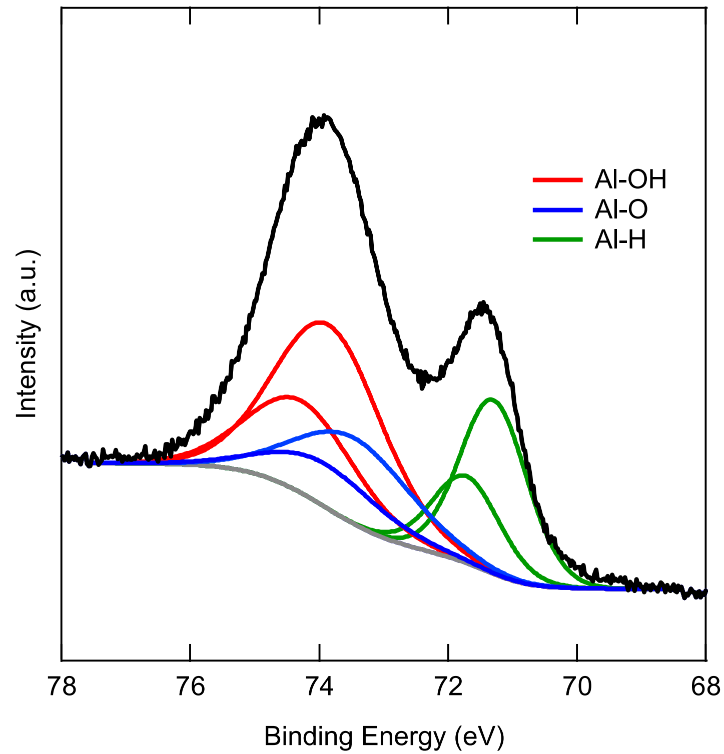




O 1s loses most metal-oxide character, forms more adsorbed hydroxide when desorbing H_2

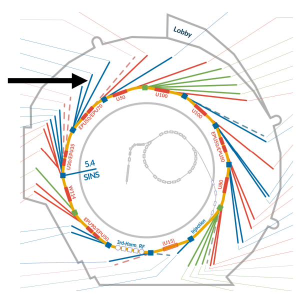
Oxidation on Recrystallized $NaAlH_4$





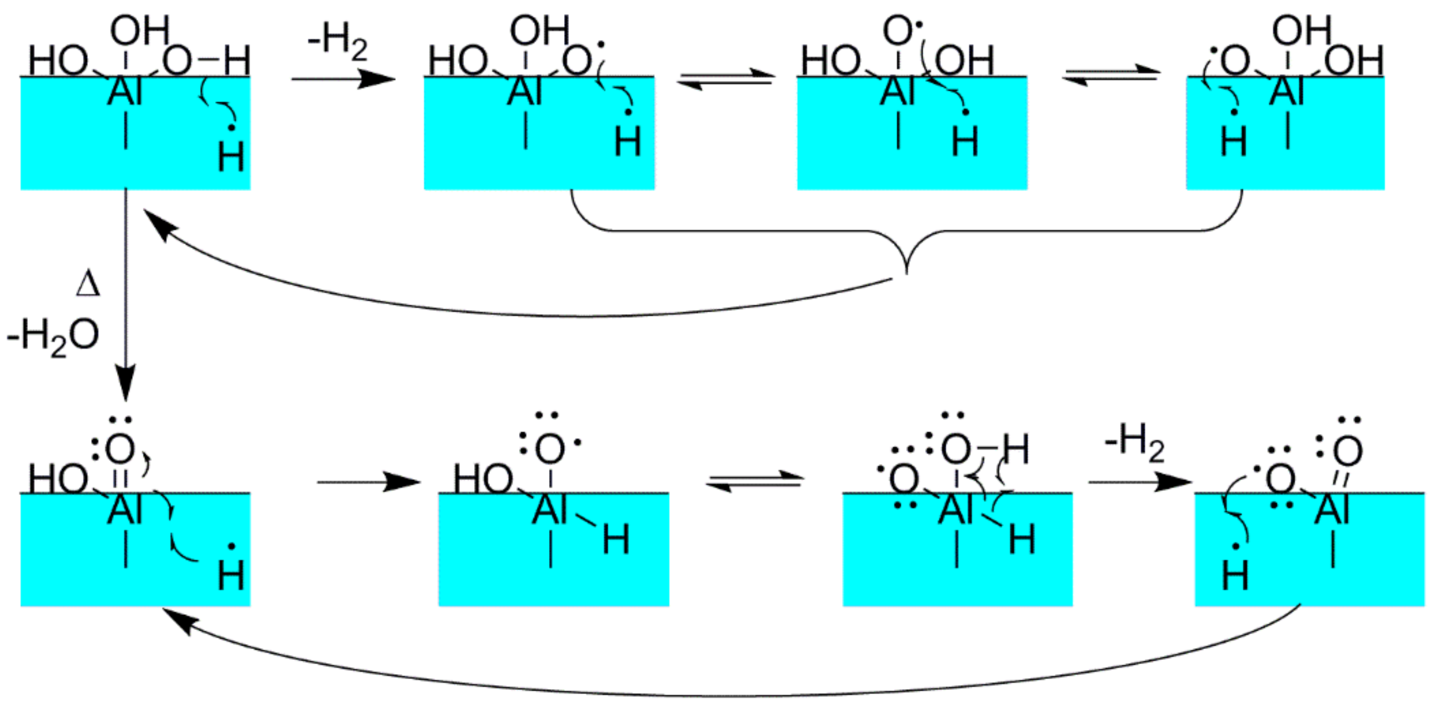
XAS (TFY) of recrystallized matches simulated (pure) spectrum

At BL 6.3.1



Y.-S. Liu

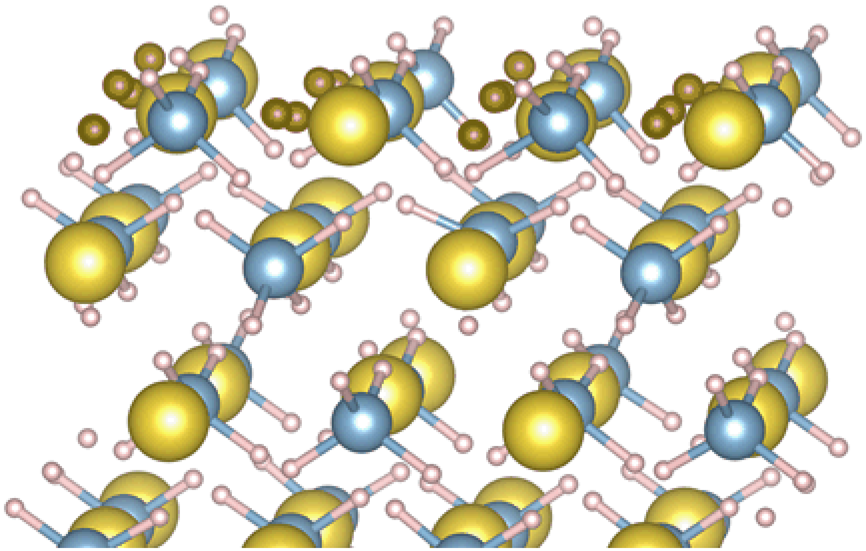
Proposed Mechanism

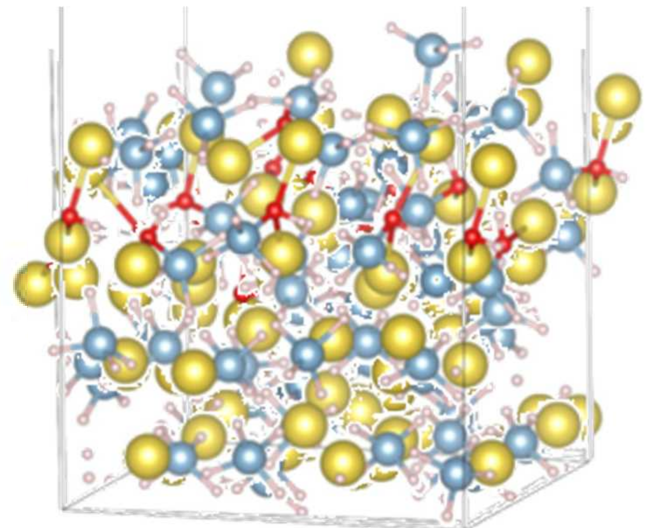


Surface Subsurface/bulk

Ḣ = H atom on AlH_4^-

Ab initio Molecular Dynamics (AIMD)



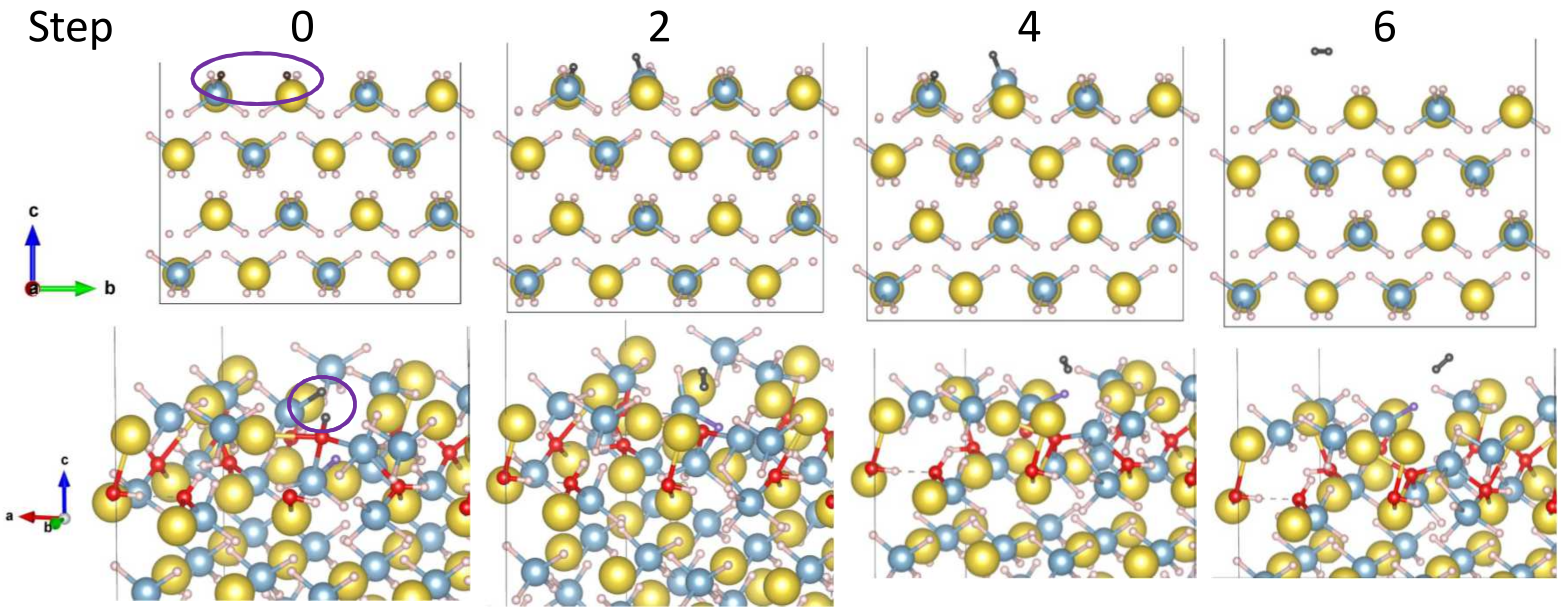


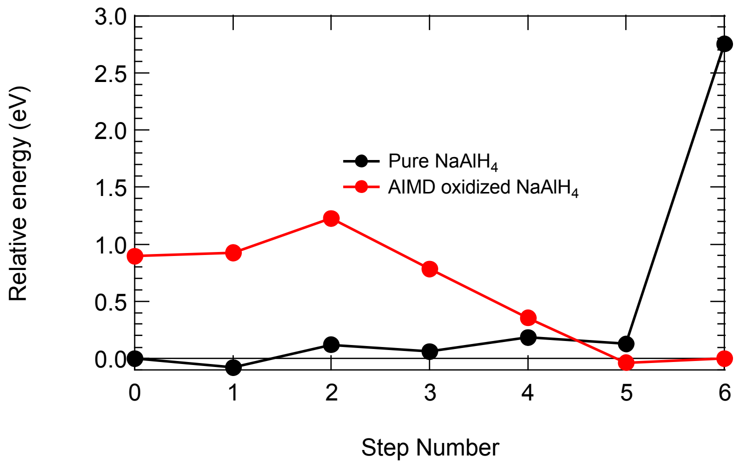
400 fs

DFT-relaxed (001) $NaAlH_4$ at 500 K

A. Rowberg, T. Ogitsu

Nudged Elastic Band Simulations

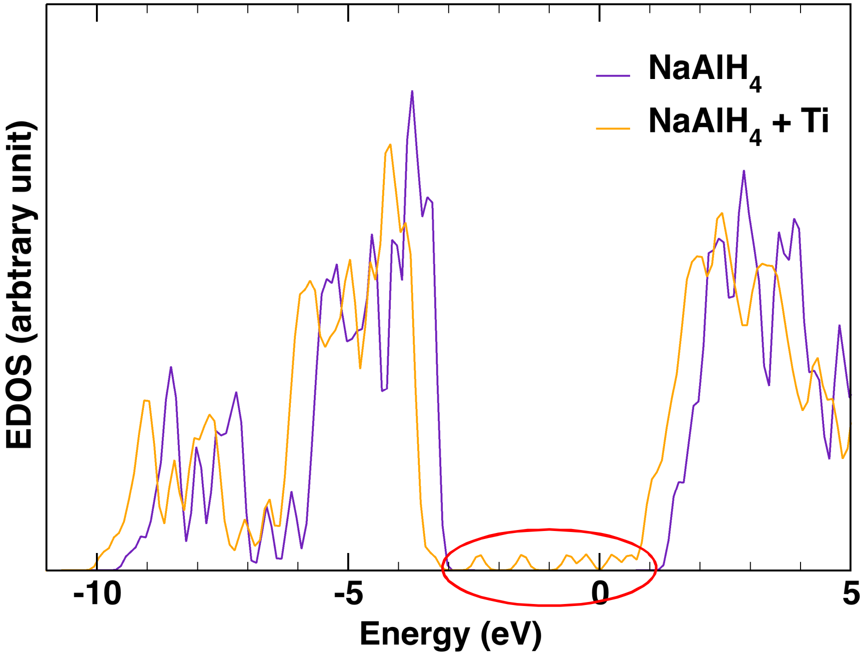




	Barrier (eV)	ΔE (eV)
Pure	2.75	2.75
Oxidized	0.34	-0.89

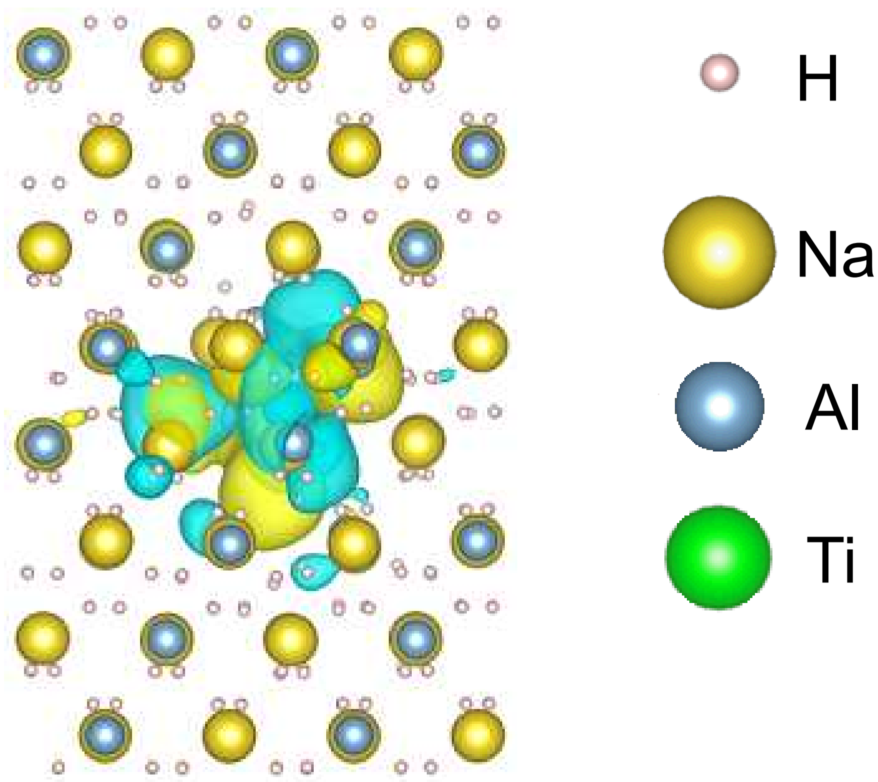
A. Rowberg, T. Ogitsu

Non-surface Role of Ti?



Ti dopant forms gap states

Delocalized enough to serve as electron reservoirs



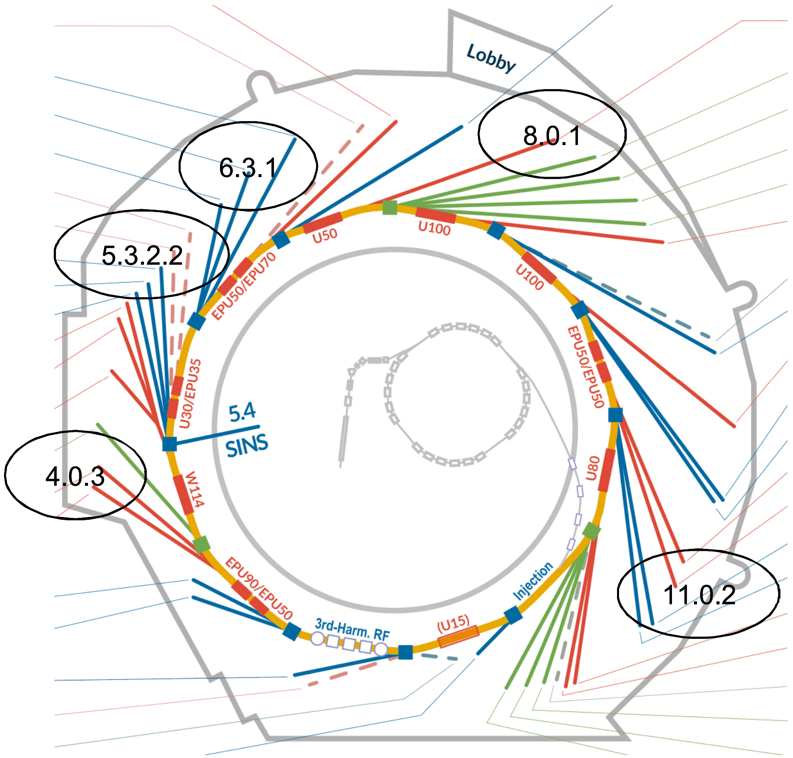
T. Ogitsu

Important Questions for Hydrides

- Reaction mechanism(s)
  - Intermediate species
  - Kinetics and rates
  - Influence of “catalytic” additives (e.g., Ti) or unavoidable impurities (e.g., O and OH)
- Cycle life
  - Contamination/poisoning
  - Buildup of (meta)stable intermediates
- How best to study realistic materials
  - *In operando* experiments-numerous requirements
  - Well-informed theoretical models

In operando Studies

- Large flux for rapid observations
- High degree of cleanliness
  - Si_3N_4 window sandwiches for STXM
  - Clean transfer to (AP)XPS, XAS, LEIS
- *In situ* techniques at elevated P, T
- Ability to probe variety of elements and their environments (chemical and spatial)



Conclusions

- Highly dynamic dehydrogenation of $NaAlH_4$ was observed
- Oxidic species likely play substantial role in desorption mechanism
- Titanium not near surface during H_2 loss
- Cleanliness difficult to achieve
- Wide suite of ALS tools/beamlines were employed for *in* and *ex situ* measurements
- High flux and variable temperature essential for studies
- Many new questions and realms of study in hydride mechanisms

HyMARC Collaboration and Funding Partners

Sandia National Laboratories

Farid El Gabaly
Robert Kolasinski
Vitalie Stavila
Mark Allendorf

Lawrence Livermore National Laboratory

Tadashi Ogitsu
Andrew Rowberg
Jonathan Lee
Brandon Wood

BERKELEY LAB
Lawrence Berkeley National Laboratory

ALS
ADVANCED LIGHT SOURCE

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David Prendergast

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