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Roles of Titanium and Oxygen at the Surface in the Dehydrogenation of Titanium-Doped Sodium Aluminum Hydride

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Background and Abstract

Ti-doped $NaAlH_4$ (sodium alanate) is a reversible hydrogen storage material with an effective capacity of 5.6 wt%, which can be cycled below 200 °C in two steps.[1] Many studies have investigated the role of Ti in its mechanism of action, with no consensus.[2] The content and behavior of the surface is critical in solid-gas reactions; thus, it is essential to investigate realistic, rather than sputter-cleaned or idealized, hydride materials *in operando.* Trace amounts of highly surface-localized oxidic contaminants have typically been ignored or assumed to be passive.[3] Through the use of *in situ* surface analysis during desorption, substantial changes in the speciation of oxygen atoms attached to aluminum were instead observed, indicating significant activity and a likely involvement of O in the dehydrogenation, whereas Ti, absent from the surface, can play no direct role.

$$3\ NaAlH_4 \rightleftharpoons Na_3AlH_6 + 3\ Al + 3\ H_2$$
$$Na_3AlH_6 \rightleftharpoons 3\ NaH + Al + \tfrac{3}{2}\ H_2$$

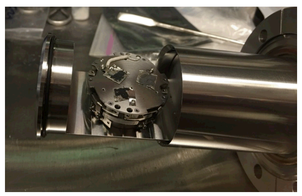
Experimental Methods

Preparation and Treatment of Material

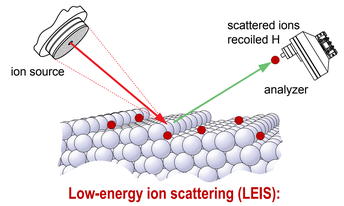
- Recrystallized $NaAlH_4$ in THF to remove Al and oxidized impurities
- High-energy ball-milled for 2 h with 10 mol% $TiCl_3$, yielding dark gray powder
- Dehydrogenated and rehydrogenated 3 times to yield realistic, cyclable material

Analysis

- Mounted powder on Pb alloy substrate for support and grounding
- Clean transfer from Ar glovebox to UHV chambers
- *In operando* AP-XPS conducted at BL11.0.2. at the Advanced Light Source, LBNL
- *In operando* low-energy ion scattering and *ex situ* XPS measurements at Sandia

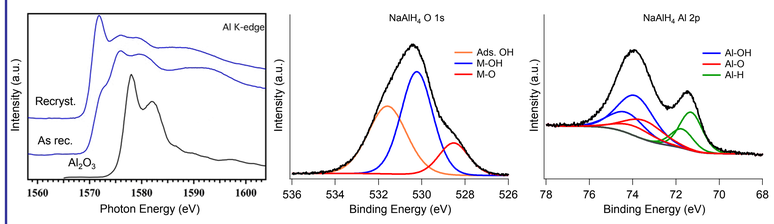


XPS Clean Transfer Holder
Compatible with both Sandia and ALS XPS systems



Low-energy ion scattering (LEIS):
Directly detect H, surface conc. of other elements (first monolayer only)

Recrystallized $NaAlH_4$-Presence of Oxide

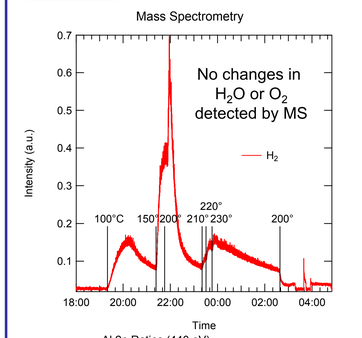


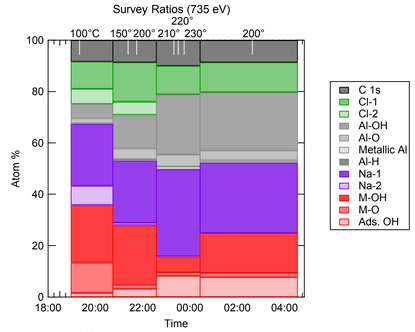
X-ray absorbance spectrum shows removal of oxidized impurities present in material as-received.
More surface-sensitive XPS found substantial oxygen content, in addition to Al-H,[4] even on clean-transferred recrystallized material.

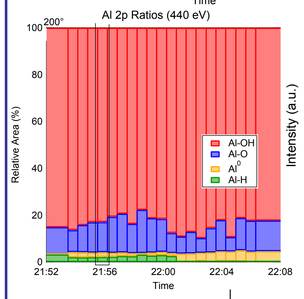
Surface oxidation not preventable; observation requires highly surface-sensitive techniques.

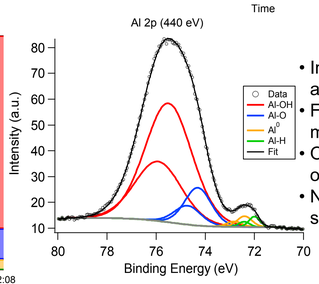
In Operando Surface Science of Hydrogen-Desorbing Ti-Doped $NaAlH_4$

AP-XPS



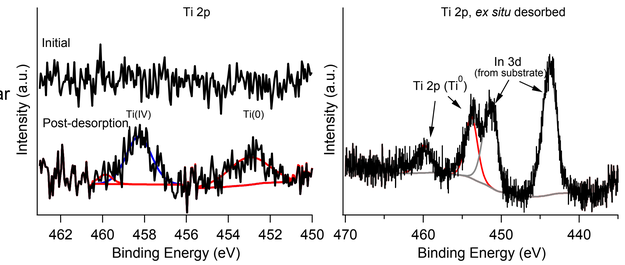




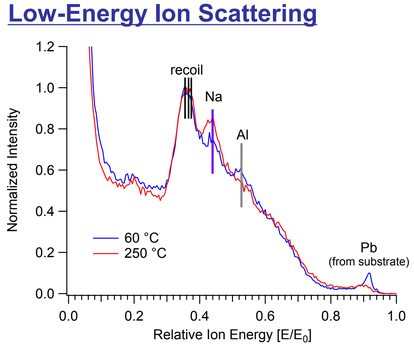


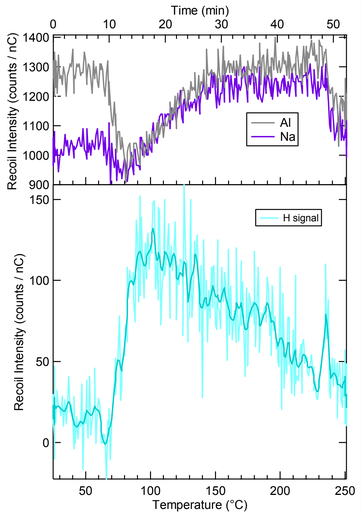
- Initially much less Al than Na at surface, then increases
- Four Al species detected at maximum desorption
- O speciation shifts from oxide to ads. OH
- No titanium detected in surveys, even at 10 mol%

- Ti not present at surface before or during H desorption
- Small amounts appear after complete desorption, both *in operando* and when desorbed *ex situ*
- Metallic and oxidized Ti present at end



Low-Energy Ion Scattering



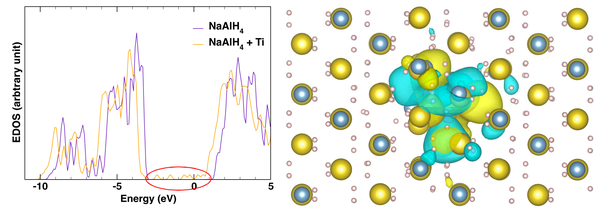


- Again no Ti detected at surface by Auger spectroscopy or ion scattering
- Surface becomes enriched with Na during heating, and Al becomes depleted
- H migrates to surface even below desorption temperature

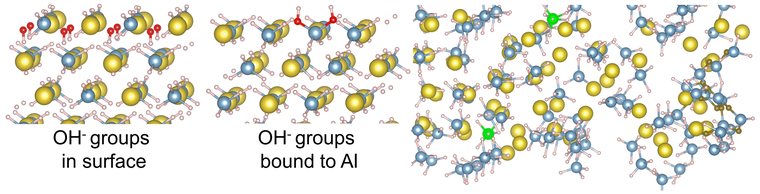
Absence of Ti at surface indicates no role in desorption, whereas dynamic O behavior suggests it is highly active in the process.

Computations of Ti-Doped $NaAlH_4$ with Oxygen

EDOS Shows Ti Enhances Conductivity through Gap States

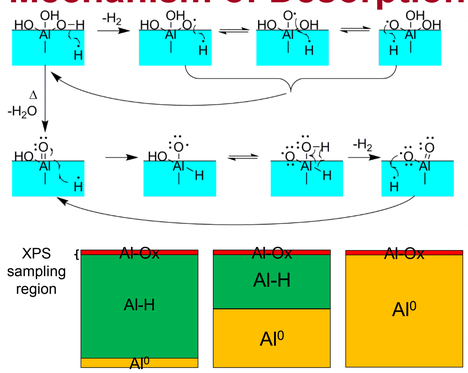


MD-Generated Surface Configurations for XPS Simulation



Delocalized states from Ti may aid in movement of electrons with hydrogen. Various O-containing species are stable at the $NaAlH_4$ (001) surface at 500 K.

Mechanism of Desorption at the Surface



- **H atoms migrate from bulk to surface, then react with catalytic Al-O species to form Al-OH, ads. OH, and H_2.**
- **Al-O bonds and Ti states act as electron reservoirs.**
- **Al-H, with little Al^0, is present at surface until desorption is almost complete suggests Al^0 phase propagates from bulk to surface.**
- **H_2 formation more facile at oxidized surface than from AlH_4^- clusters directly.**

Summary and Conclusions

- Realistic, cyclable $TiCl_3$-doped $NaAlH_4$ was prepared and analyzed by XPS and LEIS.
- The oxygen XPS spectrum was highly dynamic, shifting from more oxidized Al-O to more reduced Al-OH and adsorbed OH species as hydrogen desorbed.
- Formation of dehydrogenated phases propagates outward from the bulk toward the surface, with high Al-H concentrations remaining until near the end of desorption.
- No titanium was present at the surface, even at the high doping level of 10 mol%, until after desorption had completed. Ti thus cannot play a direct role in H_2 desorption.
- Computations indicate that oxidized Al species are stable on the surface and that titanium may have important electronic effects in the subsurface and bulk of $NaAlH_4$.

References:

[1]Bogdanović and Schwickardi, *J. Alloys Compd.* **1997**, *253-254*, 1-9.
[2]Frankcombe, *Chem. Rev.* **2012**, *112*, 2164-2178.
[3]Léon, Schild, and Fichtner, *J. Alloys Compd.* **2005**, *404-406*, 766-770.
[4]Do, McIntryre, Harshman, Lundy, and Splinter, *Surf. Interface Anal.* **1999**, *27*, 618-628.

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