Catalytic Effect of Zr and Hf on Hydrogen Absorption/Desorption of $NaAlH_4$ and $LiAlH_4$

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INTRODUCTION

Solid State Hydrogen Storage for onboard fuel cell

Targets by DOE

- High capacity : > 5.5 H/M wt%
- Low desorption temperature :60 - 100 °C
- Fast kinetics
- Long cycle time

Sodium alanate

$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2$ (3.8 wt% at 185 - 230 °C)

$Na_3AlH_6 \longrightarrow 3NaH + Al + 3/2H_2$ (1.8 wt% at 230 °C)

Total theoretical storage capacity = 5.6 wt% hydrogen

Lithium alanate

$3LiAlH_4 \longrightarrow Li_3AlH_6 + 2Al + 3H_2$ (5.3 wt% at 160 °C)

$Li_3AlH_6 \longrightarrow 3LiH + Al + 3/2H_2$ (2.6 wt% at 200 °C)

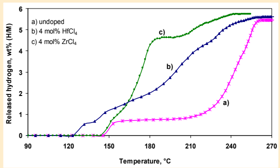
Total theoretical storage capacity = 7.9 wt% hydrogen

OBJECTIVE

- To focus on effect of transition metals (Zr and Hf) on hydrogenation /dehydrogenation of $NaAlH_4$ and $LiAlH_4$

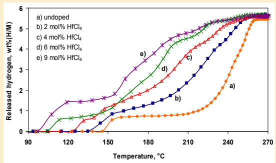
RESULTS AND DISCUSSION

1. $NaAlH_4$

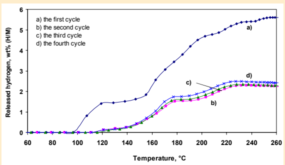


Doping transition metal on milled $NaAlH_4$ decreases temperature of decomposition and increases the kinetics.

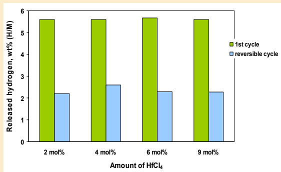
Different desorption behaviors can be observed.



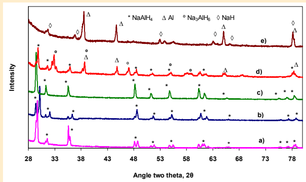
Higher amount of $HfCl_4$ doping enhances the kinetics and decreases temperature of desorption.



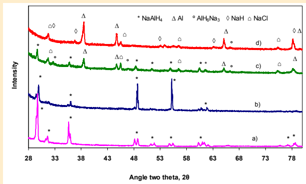
The amount of re-absorbed hydrogen drops to 2.2 – 2.6 wt% after the first desorption.



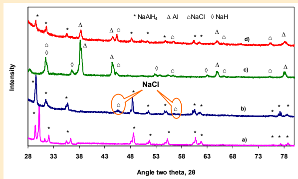
Amount of released hydrogen and absorbed hydrogen as a function of $HfCl_4$ amount.



XRD patterns of undoped $NaAlH_4$ a) as- received $NaAlH_4$ b) milled $NaAlH_4$ c) dehydrided $NaAlH_4$ at 120°C d) dehydrided $NaAlH_4$ at 196 °C e) dehydrided $NaAlH_4$ at 280°C.



XRD patterns of 4 mol% $ZrCl_4$ doped $NaAlH_4$ a) as- received $NaAlH_4$ b) milled 4 mol% $ZrCl_4$ doped $NaAlH_4$ c) rehydrided 4 mol% $ZrCl_4$ doped $NaAlH_4$ at 120°C d) dehydrided 4 mol% $ZrCl_4$ $NaAlH_4$ at 280 °C



XRD patterns of 4 mol% $HfCl_4$ doped NaAlH4 a) as- received $NaAlH_4$ b) milled 4 mol% $HfCl_4$ doped $NaAlH_4$ c) rehydrided 4 mol% HfCl4 doped $NaAlH_4$ at 120°C d) dehydrided 4 mol% $HfCl_4$ doped $NaAlH_4$

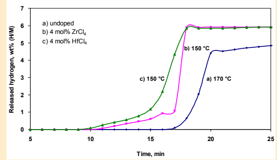
There is NaCl during the milling of $HfCl_4$ and $NaAlH_4$:

White powder ⟶ Gray powder.

And there is a change in the transition state:

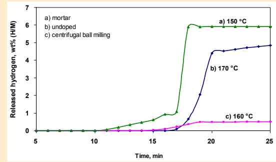
$Hf^{4+} \longrightarrow Hf^{3+}$ or Hf^{0}.

2. $LiAlH_4$

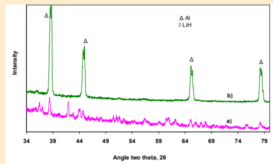


Doping transition metal on milled $LiAlH_4$ decreases temperature of decomposition and increases the kinetics.

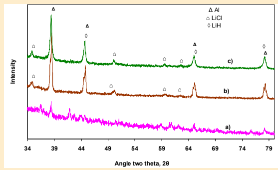
Again, different desorption behaviors can be observed.



Low stability of $LiAlH_4$ easily causes the release of hydrogen by centrifugal ball milling.



XRD patterns of a) as- received $LiAlH_4$ b) dehydrided $LiAlH_4$ at 170 °C.



XRD patterns of a) as- received $LiAlH_4$ b) dehydrided 4 mol% $ZrCl_4$ doped $LiAlH_4$ at 150 °C c) milled $LiAlH_4$ by using centrifugal ball mill.

PROCEDURE

1. Sample preparation

Metal hydride : $NaAlH_4$ $LiAlH_4$

Doped metal species : $HfCl_4$ $ZrCl_4$ (0-9 mol%)

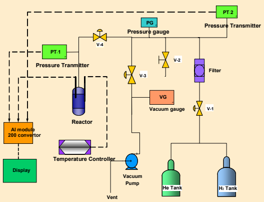
Doping method : Mortar, Centrifugal ball mill

2. Condition

Desorption : Room temperature - 270 °C

Absorption : 11 MPa 120 °C

3. Experimental set up



CONCLUSIONS

- Doping $HfCl_4$ and $ZrCl_4$ on $NaAlH_4$ improved the desorption kinetics and also decreased desorption temperature. Only 40% of hydrogen can be reabsorbed on the catalyzed $NaAlH_4$.
- Mixing $NaAlH_4$ with $HfCl_4$ by ball mill resulted in a solid state reaction.
- Doping $ZrCl_4$ and $HfCl_4$ on $LiAlH_4$ enhanced the kinetics of desorption and hydrogen capacity is up to 6 wt% but rehydriding on $LiAlH_4$ was not observed with any of the transition metals.

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