Effects of point defects and impurities on kinetics in NaAlH$_4$

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Sodium Alanate

• Viable hydrogen storage material (5.6 wt%)
  \[ \text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \]
  \[ \text{Na}_3\text{AlH}_6 \leftrightarrow 3 \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \]

• But: reactions slow
  – Only happen at too high temperature

• Addition of transition metals (Ti) was found to speed up kinetics
  – Explanation?
Hydrogen in storage materials

• **Calculations of bulk properties**
  – Formation enthalpy, …
  – Valuable information, but does not directly address kinetics

• **How does dehydrogenation take place?**
  – “One hydrogen at a time”
  – Imagine fully hydrogenated material as starting point

• **Treat hydrogen as a “defect”**
  – Move one hydrogen
    » Hydrogen interstitial
    » Hydrogen vacancy
  – Point defects well known to be involved in diffusion
  – May also serve as nucleation sites for new phases

• **Study with first-principles computations**
  – Formation energies
    » Likelihood of a certain defect occurring
  – Diffusion
Calculations

- **Density functional theory (DFT) (VASP)**
  - Generalized gradient approximation (GGA) for exchange-correlation
  - Projector augmented wave (PAW) pseudopotentials
  - VASP

- **Plane-wave expansion with cutoff 450 eV**

- **96-atom supercell geometry**
  - 2 x 2 x 2 k-point grid

- **NaAlH₄**:
  - Insulator, $E_g = 4.75$ eV (GGA); 6.9 eV (quasiparticle calculation)
  - Formation enthalpy: -48.9 kJ/mol H₂
Formalism

- $E_{\text{form}}$: formation energy
  
  **Concentration:**
  
  $$C = N_{\text{sites}} \exp \left[ -\frac{E_{\text{form}}}{kT} \right]$$

- **Example: Hydrogen interstitial**
  
  $$E_{\text{form}}(H_i) = E_{\text{tot}}(\text{NaAlH}_4:H_i) - E_{\text{tot}}(\text{NaAlH}_4) - \mu_H$$
  
  $\mu_H$: energy of hydrogen in reservoir, i.e., H chemical potential
Hydrogen defect in an insulator

- **Fermi level**
- **Conduction Band**
- **Valence Band**
- **Empty states**
- **States filled with electrons**
- **Hydrogen-induced level**
Formalism

• $E_{\text{form}}$: formation energy
  Concentration:
  \[ C = N_{\text{sites}} \exp \left[ - \frac{E_{\text{form}}}{kT} \right] \]

• Example: Hydrogen interstitial
  \[ E_{\text{form}}(H_i) = E_{\text{tot}}(\text{NaAlH}_4:H_i) - E_{\text{tot}}(\text{NaAlH}_4) - \mu_H \]
  $\mu_H$: energy of hydrogen in reservoir, i.e., H chemical potential

• H interstitial in positive charge state
  \[ E_{\text{form}}(H_i^+) = E_{\text{tot}}(\text{NaAlH}_4:H_i^+) - E_{\text{tot}}(\text{NaAlH}_4) - \mu_H + \mu_e \]
  $\mu_e$: energy of electron in its reservoir, i.e., the Fermi level

• H interstitial in negative charge state
  \[ E_{\text{form}}(H_i^-) = E_{\text{tot}}(\text{NaAlH}_4:H_i^-) - E_{\text{tot}}(\text{NaAlH}_4) - \mu_H - \mu_e \]
Hydrogen interstitials in NaAlH$_4$
Hydrogen vacancies in NaAlH$_4$

- Remove a hydrogen atom: create a vacancy

![Graph showing formation energy vs Fermi level](image)

$V^+_{H}$ without relaxation
Interstitials and Vacancies

- $H_i$ and $V_H$ simultaneously present
- Charge neutrality!
  - Equal number of $+$ and $-$ defects

$E_{\text{form}}(V_H^+) = E_{\text{form}}(H_i^-) = 0.81$ eV

At 100 °C:
$c(V_H^+) = c(H_i^-) \approx 10^{11}$ cm$^{-3}$
Titanium

- Most stable on Al site
- Can occur in different charge states

$\varepsilon(+/−)$

$\mu_e$ “pinned” at position where $+$ and $-$ have equal formation energies

(irrespective of Ti concentration, as long as exceeds defect concentration)

$\mu_e = \varepsilon(+/−) = 3.41 \text{ eV}$
A note on formation energies...

- Some papers in the literature seem to (implicitly or explicitly) assume that if a calculated formation energy is positive, the impurity will not incorporate.

- This is not correct. Remember:

\[ C = N_{\text{sites}} \exp \left[ - \frac{E_{\text{form}}}{kT} \right] \]

- A finite positive formation energy can lead to a finite concentration.

- In fact, if the formation energy were negative, the material would be unstable in the presence of the impurity!
Interstitials & Vacancies and Titanium

- Presence of Ti shifts $\mu_e$ away from $\mu_e^{\text{int}}$
- Lowers formation energy of the defects!

$$\varepsilon(+/−) \Rightarrow \mu_e \text{ “pinned” at 0.44 eV higher value}$$

$$E_{\text{form}}(H_i^-) = 0.81 - 0.44 \text{ eV} = 0.37 \text{ eV}$$

At 100 $^\circ$C:
$$c(H_i^-) \approx 10^{17} \text{ cm}^{-3}$$
(6 orders of magnitude higher than without Ti!)
Diffusion

- Once the defects are created, they can move very fast
- Calculations of diffusion barriers
Enhancement of kinetics

- Ti: electrically active
  - shifts the Fermi level
  - lowers formation energy of hydrogen-related defects (H\textsubscript{i}\textsuperscript{-})
  - increases the concentration of the defect
  - increase in self-diffusion
  - allows achieving a given concentration of defects at a lower temperature
Enhancement of kinetics

• Typically several mol % of Ti are added (>10^{20} \text{ cm}^{-3})
  – Only small fraction of added Ti is needed to achieve the effect!
  – Adding Ti adversely affects the hydrogen weight capacity.

• Experimentally:
  – Several Ti-related species have been detected
  – Only a minute fraction of the total Ti produces the observed enhancements
  – Ti-Al alloy formation
    » Presence of these alloys is not required in order to achieve a significant enhancement in the kinetics of the alanate

• Adding large amounts of Ti is unnecessary
Enhancement of kinetics

• Kinetics of hydrogen-related point defects is intimately tied to the decomposition reaction
  – Decrease in the activation energy for hydrogen diffusion: $\Delta\mu_e = 0.44 \text{ eV} = 42 \text{ kJ/mol}$
  – Experimentally observed change in activation energy for Ti-doped alanate compared to pure alanate: $\sim 40 \text{ kJ/mol}$

• Enhancement is independent of the amount of added Ti
  – …as long as the Ti$_{Al}$ concentration exceeds the concentration of hydrogen-related defects
Defect Geometry

• Hydrogen-related defects induce large changes in lattice geometry
• May serve as nucleation sites for formation of new phases
Hydrogen vacancies

- $V_H^+$: formation of two planar AlH$_3$ complexes with a H atom in between

- $V_H^-$: structural rearrangements much smaller
Hydrogen interstitials

$H_i^-$

$H_i^+$
Conclusions

• Point defects play important role in kinetics of NaAlH$_4$
  – Vacancies, interstitials
  – Mediate hydrogen transport
  – Large structural relaxations
  – Charged
  – Formation energies changed due to doping with transition metals
  – Consistent with observed effects of Ti, Zr incorporation

• References: