Formation and migration of native defects in complex hydrides

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4. Summary
1. Introduction

- Transportation takes up large amount of petroleum consumption
- Vehicle is a significant source of CO$_2$ emission

The development of new, environmental-friendly, sustainable energies for automobile is essential.
Requirement for hydrogen storage materials

- Gravimetric & volumetric density
  \[ \geq 6 \text{ wt}\% H_2, \quad \geq 45\text{g H}_2/\text{L} \]

- Operation temperature and pressure
  \(-45 \text{ to } 85 \, ^\circ\text{C}, \quad 0.4 \text{ to } 10 \text{ Mpa}\)

- Kinetics
  \[ \geq 0.02 \,(\text{g H}_2/\text{s})/\text{kW} \]

- Low Cost
Candidate hydrogen storage materials

- **Conventional metal hydrides**
  - NaNi$_5$H$_x$, VH$_2$ : gravimetric density is too low!
  - MgH$_2$, AlH$_3$ : thermodynamics of H bonding is either too strong (MgH$_2$) or too weak (AlH$_3$)!

- **Complex hydrides:** *Kinetic issue of NaAlH$_4$!*
  - NaAlH$_4$, LiBH$_4$, LiNH$_2$ : high gravimetric and volumetric density, bad reversibility and sluggish kinetics.

- **Sorbent**
  - Carbon-based materials: nonotube, fullerence, graphene, etc.
  - Metal–organic frameworks (MOFs)
    - lightweight, revisable.
    - weak physisorptive interaction
    - operation at very low temperature
Features of complex hydrides

- Composed of metal cations and H-containing “complex” ($BH_4^-$, $AlH_4^-$ and $NH_2^-$) which H atoms being covalently bonded to central atoms.
- Desorption and adsorption of H: via chemical reactions
- Release and uptake of H: by migration of H-related defects and constituent elements
- High gravimetric and volumetric density
- High temperature & sluggish kinetics for release of H

Formation and migration of H vacancy in Na$_3$AlH$_6$
2. Computational methods

- Defects are modeled using the supercell method
- GGA of Perdew and Wang for exchange-correlation
- Projector augmented wave for electron-ion interaction
- Plane-wave expansion for wave function
- Nudged elastic band method for the determination of minimum energy path and activation energy
- VASP code
Calculation of formation energy for defect

\[
E_f(H^q) = E_{tot}(H^q) + n\mu_H - E_{tot}(\text{bulk}) + q(\varepsilon_F + E_{VBM})
\]

\[
E_{VBM} = E_{VBM}^{\text{perfect}} + (V_{av}^{\text{defect}} - V_{av}^{\text{perfect}})
\]

\[
\Delta V = V_{av}^{\text{defect}} - V_{av}^{\text{perfect}}
\]

\(E_{tot}(H^q)\) and \(E_{tot}(\text{bulk})\) are the total energies of supercell with and without defect \(H\) in the charged state \(q\), respectively. 
\(\mu_H\): the chemical potential of \(H\).
\(\varepsilon_F\): the Fermi energy.
\(\varepsilon_{VBM}^{\text{perfect}}\): the valence band maximum of the perfect supercell.
\(\Delta V\): shift for the electrostatic potential between perfect supercell and the supercell with defect.

1. C. Van de Walle and J. Neugebauer, J. Appl. Phys. 95, 3851 (2004);
Nudged Elastic Band Method (NEB)

Fig. (a) Schematic illustration of Minimum Energy Path (MEP) on the potential energy diagram between two equilibrium positions (solid lines). (b) Schematic illustration of NEB determined MEP.

3. Formation and migration of H vacancy in Na$_3$AlH$_6$

- Point defect motion with an activation energy of 0.126 eV by anelastic spectroscopy measurement of NaAlH$_4$.

- The identification for the mobile species is controversial
  - May be H vacancy in Na$_3$AlH$_6$ (Palumbo et al., J. Phys. Chem. B 109, 1168 (2005))

- Energetically favorable defects in semiconductor and insulator are probably in charged states.
  - Previous theoretical works for hydrogen dynamics in Na$_3$AlH$_6$ were exclusively performed on neutral H vacancy.
  - Previous first-principles studies on the diffusion in NaH, MgH$_2$ and NaMgH$_3$ revealed that the charged defects dominate the diffusion process
  - (S. Hao and D. S. Sholl, Appl. Phys. Lett. 93, 251901 (2008))

This work: $V_{H}^{0}, V_{H}^{+}, V_{H}^{-}$
Structure of Na₃AlH₆

**Calculation:**
- a = 5.352 Å, b = 5.529 Å, c = 7.703 Å, and β = 89.88°

**Experiment:**
- a = 5.359 Å, b = 5.507 Å, c = 7.702 Å, and β = 89.72°

**Primitive cell**
- Monoclinic: P21/n

**2x2x1 supercell**
Geometries of AlH$_6$, AlH$_5$ units and Na$_3$AlH$_6$ supercell

(a) AlH$_6$ unit
(b) AlH$_5$ unit: $V_H^0$
(c) AlH$_5$ unit: $V_H^-$
(d) AlH$_5$ unit: $V_H^+$

(b) Minimum change for the structure of AlH$_5$ complex with creation of $V_H^0$

Dramatic change for the structure of AlH$_5$ complex with creation of $V_H^+$ or $V_H^-$

(c) The closest four H atoms relax away from Va

(d) The closest four H atoms relax toward Va.

Fig. 1 Relaxed geometries of AlH$_6$ and AlH$_5$
Formation energy for defect

Fig. 2 Formation energies for three types of H vacancies as a function of the Fermi energy.

- Formation energy for $V_H^0$ is higher than that of charged vacancy for any position of the Fermi level.

- Thermodynamic transition level ($-/+)$ for H vacancy is 1.36 eV when the charge neutrality is enforced.
**Diffusion barrier**

**Fig. 3** (a) local diffusion path (b) non-local diffusion path

**Fig. 4** The minimum energy paths for local and non-local diffusions of three types of hydrogen vacancy in Na$_3$AlH$_6$

$V^0_H = 0.42$ ev (This work), 0.41 ev (literature)
Discussion

- Point defect motion with an activation energy of 0.126 eV by anelastic spectroscopy measurement of NaAlH$_4$

- The identification for the mobile species is controversial
  1. May be H vacancy in Na$_3$AlH$_6$
  2. Na vacancy diffusion
  3. H vacancy non-local diffusion
The activation energy for Na vacancy from a 2e to a 4b site alone cannot account for the experimentally observed mobile species.

Table 1

<table>
<thead>
<tr>
<th>Diffusion Path</th>
<th>Activation Energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>4e→2b</td>
<td>a 0.09 (0.12)</td>
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<tr>
<td>2b→4e</td>
<td>0.33</td>
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Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>Formation Energy (eV)</th>
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<tbody>
<tr>
<td>H</td>
<td>1.51</td>
</tr>
<tr>
<td>4e-Na</td>
<td>3.06</td>
</tr>
<tr>
<td>2b-Na</td>
<td>2.82</td>
</tr>
</tbody>
</table>

This work

Diffusion barrier

Formation energy of $V_{H}^0 = 1.51$ ev

Diffusion barrier of $V_{H}^+ = 0.1$ ev

Experimental value = 0.126 ev

Fig. 5 The minimum energy paths for local and non-local diffusions of three types of hydrogen vacancy in Na$_3$AlH$_6$

- The observed mobile species is probably positive H vacancy in the form of local diffusion.
4. Conclusion

1. Formation and diffusion events of H vacancies with neutral and charged states in Na$_3$AlH$_6$ were studied.

2. The diffusion barrier for local mechanism is smaller than that of non-local for all three types of H defects, and H diffusion in Na$_3$AlH$_6$ is dominated by mobility of V$_H^+$. 

3. The observed highly mobile species in anelastic spectroscopy experiment for NaAlH$_4$ is probably V$_H^+$ in the form of local diffusion.

References:

Thank you for your attention!

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