The Role of Impurities in the Complex Hydrides

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Objectives and Overview

I. Fundamental Limitations
   – density of hydrogen and desorption enthalpy

II. Open Questions in Complex Hydrides
   – growing consensus on reversibility mechanism in NaAlH$_4$
   – important discoveries with unresolved issues in alanates
   – *illustrate the dramatic role of impurities*
   – *provide ideas for basic research*
   – nanoscale confinement and controlling surface chemistry in borohydride and amide/imide systems
Hydrogen Density in Metal Hydrides

<table>
<thead>
<tr>
<th>Compound</th>
<th>H/M</th>
<th>Å³ / H atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice gas</td>
<td>~0.01</td>
<td>large</td>
</tr>
<tr>
<td>LaNi₅H₆</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>LiH</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>TiH₂ or VH₂</td>
<td>2</td>
<td>~10</td>
</tr>
<tr>
<td>MgH₂</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>NaAlH₄</td>
<td>2</td>
<td>17</td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>2.7</td>
<td>14</td>
</tr>
<tr>
<td>solid H₂</td>
<td>--</td>
<td>19 (38 per H₂)</td>
</tr>
<tr>
<td>liquid H₂</td>
<td>--</td>
<td>22.5 (45 per H₂)</td>
</tr>
</tbody>
</table>

DOE target 7.5 wt.% and 70g/liter

= 24 Å³ / H atom

- New materials are unlikely to exceed these densities

Interstitial hydrides are easily ‘tunable’
- H embedding energy in homogeneous e⁻ gas has a minimum around $n_0=0.01/a_0^3$ [J. K. Norsk, Phys. Rev. B, 26, 2875 (1982)]
- electron density determines the chemical potential
- vary the volume and chemistry of interstitial site
- alloying easy, can adjust plateau pressure

Complex ionic hydrides are NOT
- electrostatically dominated cohesive energy
- atomic radii important for structural stability
- alloying more difficult (example: NaCl, NaF)
Phase Segregation On Decomposition Introduces Several Problems

- Multiple phases with complex interfaces
- Mass transport problems
- Complicated engineering considerations
Reversibility in Ti-doped NaAlH$_4$
Titanium Dopant Goes with the Aluminum on Decomposition of NaAlH₄

Sample Preparation
- 3:1 molar ratio
- NaAlH₄ : TiCl₃
- mechanically milled
  (33 mol.% loading)

TiAl₃ standard
- Ti:Al₃
- mechanically milled
- L1₂ structure
- 7 nm coherence length

Desorbed Sample Al (111) reflection asymmetry due to Ti

AlH$_x$ Formation Occurs on Al (111)
Surface and is Mobile

- Requires atomic H
- Subsurface Ti in Al lowers barrier for H$_2$ bond dissociation
Mass Transport in NaAlH₄ Mediated via AlHₓ and Na Vacancies

• Free energies of formation and concentrations of native defects in NaAlH₄ and Na₃AlH₆
• determined at possible two-phase interfaces

Kinetic Monte Carlo Results and transition state theory
• NaAlH₄: AlHₓ vacancies
• Na₃AlH₆: Na vacancies

Table 2. Defect Formation Energies and Concentrations in NaAlH₄ at T = 400 K, Including Vibrational and Gas-Phase H₂ Enthalpies and Entropies

Vacancy Diffusion in NaAlH₄ and Na₃AlH₆

Explanation for NaAlH$_4$
Reversibility is Incomplete

- Intermediates observed in XRD
  - X1 and X2 phases
- X1, X2 very sensitive to overpressure
- 0.1 < P < 1 or 2 bar
- These phases have never been conclusively identified
- Experiments near operating conditions are important

Discovery of Phase “S105” - Fast Al Motion In NaAlH₄

S105 first observed when heating NaAlH₄ under H₂ overpressure near the melting temperature

S105 is due to the presence of oxygen impurities. H₂O or NaOH exposure.
Monte Carlo Method (PEGS) Generally Obtains Observed Crystal Structures

- PEGS method -
Search for Intermediates in NaAlH$_4$

- gamma-NaAlH$_4$ stable above 320K
- Charged AlH$_4$ and neutral AlH$_3$ vacancies: computed barriers for diffusion are less than 0.1 eV

Cmcm and Fmm2
- Larger volume available to AlH$_4$ units
- XRD not consistent with X1, X2 phases
S105 Must Contain 4-coordinate Al

- XRD shows structure is still $I4_1/a$
- Structure factor changes only


5,6-coord Al (comp. NaAlH₄)
Oxygen Contamination? Many Hydride Preparation Techniques Introduce Impurities

- Mill type: shaker mills, planetary mills
- Ball construction: steel, WC, ceramic
- Mill wall construction: steel, WC, ceramic, etc.
- Mill seal allows for leaks – contamination from atmosphere
Effect of Oxygen in Na-Al-H?
Oxygen In Alkali Metal Hydrides

Phases of NaOH:
• low temp phase: Bmmb (orth)
• alpha-phase: P2_1/m (mono)
• beta phase: Fm3m

Q: What is the temperature dependence of the formation of solid solution phase NaH/NaOH?


Differential scanning calorimetry indicates excellent reversibility of NaH/NaOH solid solution formation.

rapid hydrogen motion
Comments

- Oxygen (OH⁻) content in NaH, NaAlH₄ will vary strongly with temperature and may have a significant impact on kinetics
- Computationally expensive to predict intermediate phases and their stability from first principles – depend sensitively on T and P (harmonic vs. quasi-harmonic, etc.)
- Test materials closer to operating conditions
- Experiments with very high purity starting materials to identify contaminant issues
- Q: Could impurity doping improve the kinetics in other interesting complex hydride systems?
Interfaces
and
Surfaces
Free Nanoparticle Stability Is a Function of Size

Predicted hydride destabilization as a function of particle size, using the Wulff construction

Free Nanoparticles in the Na-Al-H System
Majzoub, et al., JPCC, 115, 2636 (2011)

Q: How does nanoconfinement alter thermodynamics?
Benefits of Nanoconfinement

- Improves kinetics and reversibility
- Can impact thermodynamics
- Safety
- Surface functionalization allows for selectivity of reactions
- Frameworks can be active, e.g. Li intercalation in carbon
- Difficult to handle computationally -- work is needed here
Nano-confined LiBH₄ is Reversible

Enhanced Hydrogen Storage Kinetics of LiBH₄ in Nanoporous Carbon Scaffolds

Adam F. Gross, John J. Vajo,* Sky L. Van Atta, and Gregory L. Olson
HRL Laboratories, LLC, 3011 Malibu Canyon Road, Malibu, California 90265
Received: November 20, 2007; In Final Form: January 25, 2008

Ordered Nanoporous Materials

- ACS Nano, 6, 9807-9817 (2012)
Nanoconfined LiBH$_4$ is reversible and reaction pathway is changed.

**Controlled Reaction Pathway:**
Diborane Release

**Demonstrated Low Temperature Reversibility**
PCT of LiBH$_4$@NPC Indicate No Change From Bulk Thermodynamics

- 4nm NPC
- 20 wt.% LiBH$_4$
- Flat plateau
- Enthalpy: 75 kJ/mol H$_2$

Note: New sample each cycle
PCT of NaAlH$_4$@NPC Indicate A Single Step Reaction And Altered Thermodynamics

\[ \Delta H = 35 \pm 3 \text{ kJ/mol H}_2 \]

NaAlH$_4$@NPC

Vitalie Stavila
Sandia National Laboratories


DSC indicates single step for NaAlH$_4$@NPC


- Activated carbon fiber
- 0.5 – 4 nm pore size
- Melt-infiltrated
- 1800 m$^2$/g
What can we explain computationally?

• Wetting is observed for molten LiBH$_4$ (Gross, et al., J. Phys. Chem. C 2008, 112, 5651-5657)

• Can explain the wetting computationally?
High- and Low-temperature Carbonized Phenolic Resins Show Different Character and Defect Density

Harris, P.J.F., Philosophical Magazine, 2004, 84, 3159–3167

$\text{OH} + \text{HCHO} = \text{Bakelite}$  
Baekland, 1907

More sp$^2$ character

~1000°C

~3000°C

More dangling bonds

Harris, P.J.F., Philosophical Magazine, 2004, 84, 3159–3167
Model the Carbon Environment Using a Sheet of Graphene

- 7 X 7 super cell of graphene with 17 Angstrom vacuum layer
- Crude but no tractable amorphous structure models

No Wetting for LiBH$_4$ or Other Likely Decomposition Products on Graphene Sheet

- contradicts experimental observation of wetting
- Note: *Free*-nanoparticle reference energy will show wetting
Four-step Process Results in LiBH₄ Wetting of Carbon

(1) LiBH₄ → B + other stuff

(2) Partial decomposition of LiBH₄

(3) Remaining LiBH₄ will wet the carbon

(4) LiH does not wet this surface!
Experimental Confirmation via TEM

Characterization of the Dehydrogenation Process of LiBH$_4$ Confined in Nanoporous Carbon

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Supporting Information

ABSTRACT: Annealing in the transmission electron microscope allows direct comparison of the same nanoporous carbon scaffold particles following dehydrogenation of the confined LiBH$_4$. At a nominal temperature of 200 °C, a granular crust of cubic and cuboidal LiH nanocrystals ~8—15 nm wide grew on the outer surface of the scaffold. Furthermore, these crystals migrated on the carbon support film away from the scaffold. Ejection of material from the scaffold also occurred upon dehydrogenation in a differential scanning calorimeter. The form of the ejected material was different, being bristles instead of cubes or cuboids. This ejection of LiH and thus preferential segregation of lithium from boron is proposed to explain the observed continual decrease in hydrogen storage capacity with the number of cycles.

Stephen House, Ian Robertson
N-doped Carbons Through Melt-infiltration of \( \text{Li}_4\text{BN}_3\text{H}_{10} \)

Journal of Materials Chemistry A 2013, 1, 3926

Tailoring the hydrogen storage properties of \( \text{Li}_4\text{BN}_3\text{H}_{10} \) by confinement into highly ordered nanoporous carbon

Xiangfeng Liu,*ab David Peasleea and E. H. Majzoub*a

\[ \text{LiBH}_4 + 3 \text{LiNH}_2 = \text{Li}_4\text{BN}_3\text{H}_{10} \]
Nanoconfinement of Li$_4$BN$_3$H$_{10}$ Changes Enthalpy from Exothermic to Endothermic
Reversible Hydrogen Storage by NaAlH$_4$ Confined within a Titanium-Functionalized MOF-74(Mg) Nanoreactor

Vitalie Stavila,†,* Raghunandan K. Bhakta,† Todd M. Alam,‡ Eric H. Majzoub,§ and Mark D. Allendorf†,*

ACS Nano, 6, 9807, 2012
Conclusions

• Nanoconfinement alters the properties we are interested in controlling
• Limited work to date on functionalization of carbons
• Limited work to date on the vast array of MOFs available
• Computational work needed to address catalysis and interfaces
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