Hydrogen Storage in Metal-N-H Complexes

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Systems under Investigations

Amide | Imide | Nitride | Nitride Hydride
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LiNH₂ | Li₂NH | Li₃N, Mg₃N₂ | Ca₂NH
Li₂MgN₂H₂ | LiMgN | |
I. Binary Systems

TPR & TPD of Li₃N sample

\[
\text{Li}_3\text{N} + 2\text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH}
\]

I. Binary Systems

P-C-T Curves of Li-N-H

I. Binary Systems

TPR & TPD of Ca$_2$NH sample

I. Binary Systems

P-C-T curves of Ca$_2$NH

## I. Binary Systems

### Reactions

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction</th>
<th>Capacity</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₃N</td>
<td>Li₃N + 2H₂ − LiNH₂ + 2LiH</td>
<td>11.4wt%</td>
<td>323-673K</td>
</tr>
<tr>
<td>Li₂NH</td>
<td>Li₂NH + H₂ − LiNH₂ + LiH</td>
<td>7.0wt%</td>
<td>323-673K</td>
</tr>
<tr>
<td>Ca₂NH</td>
<td>Ca₂NH + H₂ − CaNH + CaH₂</td>
<td>2.1wt%</td>
<td>723-973K</td>
</tr>
</tbody>
</table>

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I. Binary Systems

Thermodynamic parameters – van’t Hoff plot

\[
\Delta H = -66.1 \text{ kJ/mol } \text{Li}_2\text{NH}
\]

\[
\Delta H = -88.7 \text{ kJ/mol } \text{Ca}_2\text{NH}
\]
Tuning the Thermodynamic Parameters

\[ \text{M-N-H}_{n+2} \leftrightarrow \text{M-N-H}_n + \text{H}_2 \]

\[ \Delta G^0 = -RT \ln K_p = RT \ln P_{\text{H}_2} \]

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]

\[ \Delta S \approx S_{\text{H}_2} \]

At \( P_{\text{H}_2} = 1.0 \text{ bar} \), \( \Delta G^0 = 0 \), thus,

\[ T = \frac{\Delta H^0}{S_{\text{H}_2}} \]

\[ \Delta H \text{ – determine the reaction temperature} \]
Mechanism – Interaction between amide & hydrides

H atoms attached to N normally possess positive charges, however, H in ionic hydrides have negative one. The strong chemical potential for the combination of $H^+$ and $H^-$ is one of the important driving forces!

By changing amide or hydride, new reactions and new materials may be discovered.
II. Ternary Systems  Li-Ca-N-H

Li-based ternary imide I – Li-Ca-N-H

\[ 2\text{LiNH}_2 + \text{CaH}_2 \rightarrow \text{Li}_2\text{CaN}_2\text{H}_n + \frac{(6-n)}{2} \text{H}_2 \]

Hydrogen desorption occurs at lower temperature for the ternary system.

II. Ternary Systems Li-Ca-N-H

Li-Ca-N-H – P-C-T curve at 220°C

Less than 2 hydrogen atoms can be reversibly stored by one ternary complex of Li-Ca-N-H, which is ~ 2.0 wt% of the starting material.

II. Ternary Systems Li-Ca-N-H

CaNH-like

Space Group No.: 164
Short Hermann-Mauguin Symbol: P- 3 M 1
Schoenflies Symbol: D3d3

Anti-La$_2$O$_3$ Structure

a = 3.56000 Å
b = 3.56000 Å
c = 5.93560 Å
Li-based ternary imides II – Li-Mg-N-H

\[
\text{Mg(NH}_2\text{)}_2 + 2\text{LiH} \rightarrow \text{Li}_2\text{MgN}_2\text{H}_2 + 2\text{H}_2 \quad 5.55\text{wt\%}
\]

Hydrogen desorption profiles of Li-Mg-N-H and Li\textsubscript{2}NH. Drastic temperature decrease in hydrogen desorption was achieved in ternary systems.

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III. Ternary Systems Li-Mg-N-H

Volumetric Release & Soak

Li-Mg-N-H – P-C-T at 180°C

P-C-T measurement shows ~ 5.5wt% of storage achieved at temperature around 180°C or below. The desorption pressure is pretty high, i.e., at 180°C, the plateau pressure is above 20 bars.

Certain hysteresis exists.

Li-Mg-N-H - Thermodynamic Analysis

Van’t Hoff plot

\[ \log(P) = \frac{-4683.65}{RT} + 13.47 \]

\[ \Delta H_{\text{des}} = 38.9 \text{ kJ/mol-H}_2 \]

Theoretically, hydrogen desorption equilibrium pressure at 90°C is 1.0 bar, close to the PEM fuel cell operation temperature.

Kissinger’s plot
\[
d\left[\ln\left(\frac{\beta}{T_m^2}\right)\right]/d\left(\frac{1}{T_m}\right) = -\frac{E_a}{R}
\]

Activation energy for hydrogen release form Mg(NH2)2+2LiH is: \(E_a = 102\text{kJ/mol-H}_2\).

For the decomposition of Mg(NH2)2, it is \(\sim 130\text{ kJ/mol}\).
Compositional Changes

\[
\text{Mg(NH}_2\text{)}_2 + n \text{LiH} \rightarrow \text{Li-Mg-N-H} + \text{H}_2 \quad n = 1, 2, 3
\]

Decrease in LiH content will lead to the release of ammonia at temperature around 200ºC.

Increase Li content further stabilizes N content in the complex and may also lead to the increase in total amount of H2 desorbed. However, part of the hydrogen could be only released at higher temperatures.
III. Ternary Systems Li-Mg-N-H

P-C-T Measurements – 220 ºC

Clearly, Li-Mg-N-H with Li/Mg=2/1 gives more usable hydrogen at lower temperature than that of Li/Mg=3/1, wherein part of the hydrogen retains in the complex until higher temperatures.
Ammonia Control

• There are competing processes involved, i.e., Desorption of H2 and direct decomposition of NH containing compounds to NH3.

• Generally, desorption of H2 is favored at lower temperatures.

• To avoid ammonia, we can either lower down the operation temperature or increase hydride content in the reactant.
IV. Other Systems Mg-Na-N-H

\[ \text{Mg(NH}_2\text{)}_2 + 2\text{NaH} \leftrightarrow \text{Na}_2\text{MgN}_2\text{H}_n + (6-n)/2\text{H}_2 \]

Desorption in the temperature range of 80 - 200°C.

Absorption: Ambient temperature or above.

-- Xiong ZT, Hu JJ, Wu GT, Chen P., J Alloy Comp, published on line
IV. Other Systems Mg-Na-N-H

P-C-T and van’t Hoff plot

\[ \Delta H = 19 \text{ kCal/mol-H}_2 \]
IV. Other Systems Mg-N-H

\[ \text{Mg(NH}_2\text{)}_2 + \text{MgH}_2 \leftrightarrow \text{MgNH (?) + H}_2 \]

More than 2.0 wt % of hydrogen was released at room temperature or below. Hard to recharge.
In summary, reversible hydrogen storage has been confirmed in the following systems –

A. \( \text{Li}_3\text{N} \)
B. \( \text{Li}_2\text{NH} \)
C. \( \text{Ca}_3\text{N}_2 \)
D. \( \text{Ca}_2\text{NH} \)
E. \( \text{Li-Mg-N-H} \) with different molar ratio of Li/Mg/N
F. \( \text{Li-Ca-N-H} \) with different molar ratio of Li/Ca/N
G. \( \text{Li-Al-N-H} \) with molar ratio of Li/Al = 3/1
H. \( \text{Mg-Na-N-H} \) with different molar ratio of Mg/Na/N
I. \( \text{Mg-Ca-N-H} \) etc..
VI. Challenges in the Practical Applications

- Chemical Instability – Competing chemical routes exist, exp. direct decomposition of reactants. Sensitive to moisture, CO₂, O₂ etc.
- Operation Temperature.
- Lifetime – sample segregation, which induces the slow kinetics.
- Material Synthesis and storage.
- Thermodynamic data.
VII. Perspectives

• Plenty systems for exploration: Nitride, Imide, Nitride hydrides etc., binary, ternary or Multinary.

• Huge room for optimization: Catalyst, Additive, Crystal dimension, Morphology etc..

• New Chemistry – New chemicals, New reactions.
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References