Novel Indirect Hydrogen Storage Materials

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Basic Research Needs for the Hydrogen Economy

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Hydrogen Storage for Vehicles

Schlapbach & Züttel, *Nature*

3.59 wt%  1.37 wt%
Direct Hydrogen Storage

- Liquefied H₂
  - Boil-off, cost of liquefying, safety
- High pressure H₂
  - Cost of compression, safety, volumetric density
- Metal hydrides, e.g. MgH₂
  - Low bulk density, kinetics
- Complex hydrides, e.g. NaAlH₄, LiAlH₄
  - kinetics/catalyst, synthesis, reversibility
- Chemical hydrides, e.g. borane-ammonia adducts
  - Expensive materials, reversibility, complex system
- Physisorption in porous materials
  - Material developments, synthesis, gravimetric and volumetric density
Indirect Hydrogen Storage

- Methane
  - reforming, reformate clean-up, volumetric density

- Methanol
  - reforming, reformate clean-up, safety

- Ethanol
  - reforming, reformate clean-up, cost

- Ammonia
  - reforming, safety
Ammonia as Hydrogen Carrier

- Dense liquid; ~ 18wt% of hydrogen
- Optimized catalyst exist
- Relatively easy to reform to H\textsubscript{2}

- But liq. NH\textsubscript{3} is normally considered too dangerous ! ! ? ?
Ammonia Storage in Ammines

\[ \text{Mg(NH}_3\text{)}_6\text{Cl}_2 \text{ (s)} \rightarrow \text{MgCl}_2 \text{ (s)} + 6\text{NH}_3 \text{ (g)} \]

Desorption temperature ramp: 10 K/min

Accumulated NH\textsubscript{3} capacity [mol NH\textsubscript{3} / mol MgCl\textsubscript{2}]

\[
\begin{array}{|c|}
\hline
\text{Temperature [K]} & \text{NH}_3 \text{ desorption rate [mol/s]} \\
0 & 1 \times 10^{-4} \\
200 & 6 \times 10^{-5} \\
400 & 4 \times 10^{-5} \\
500 & 2 \times 10^{-5} \\
600 & 1 \times 10^{-5} \\
\hline
\end{array}
\]

1\textsuperscript{st} run

2\textsuperscript{nd} run

4 : 1 : 1

New Concept for Energy Storage: using Metal Ammine Complexes

Storage unit

Integrated ammonia decomposition catalyst

Release (thermal desorption)

Mg(NH$_3$)$_6$Cl$_2$

To fuel cell

NH$_3$: “largest” chemical in the world

Hydrogen

Nitrogen

Stored as NH$_3$
The $\text{H}_2$ Pathway

Reversible!
Ammonia Decomposition is Central

\[ 2\text{NH}_3 \xleftrightarrow{} \text{N}_2 + 3\text{H}_2 \]

NH$_3$ Release from Compact Tablets: Self-generated Nanoporosity

Indirect Solid Storage – Mg(NH$_3$)$_6$Cl$_2$

<table>
<thead>
<tr>
<th></th>
<th>$E_{desorp}$</th>
<th>$E_{migr.}$</th>
<th>$E_{H-vac}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NH$_3$)Cl$_2$</td>
<td>$\sim 0.5$ eV</td>
<td>$&lt;$0.6 eV</td>
<td>$\sim 0.5$ eV</td>
</tr>
</tbody>
</table>

Hummelshøj, Christensen, Honkala, Nørskov, unpublished
Safe Hydrogen Storage!

1.5 liter $\text{H}_2$ and a lighter...
Details on the Hydrogen Capacity

“Virtual” H$_2$-pressure: $\sim$1300 bar!

Measured capacity. Not theoretical value

volumetric H$_2$ density [kg H$_2$ pr m$^3$]

gravimetric H$_2$ density [mass %]

DOE 2005
DOE 2010
DOE 2015
2nd Generation Prototype – Integrated NH₃ Decomposition

*Insulate the decomposition reactor with the storage material…*
Compact H$_2$-Producing System

H$_2$ + N$_2$

Integrated NH$_3$-decomp reactor

μ-reactor for production of H$_2$:
Sørensen, Nielsen, Jensen, Hansen, Johannessen, Quaade, Christensen, Catal. Comm., 6 (2005) 229

Traces of NH$_3$: Absorption in degassed salt (< 10ppm NH$_3$)
Summary

Current status

• High demonstrated density
  – 9.1 wt% H\textsubscript{2}; 108 kg H\textsubscript{2}/m\textsuperscript{3}
• Reversible
• Fast release kinetics
• Simple to handle in open atmosphere
• Inexpensive (ca. 0.5 €/kg)
• CO\textsubscript{2}-free energy carrier

On-going work

• Heat management
  – NH\textsubscript{3}-decomposition reactor
• Purification
  – for PEM-FC
• Packaging/recycling
Thank you for your attention