Hydrogen Generation from Ammonia for PEM Fuel Cells

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Yoshitsugu Kojima
Hiroshima University
Institute for Advanced Materials Research

Cross-ministerial Strategic Innovation Promotion Program (SIP)
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1. Energy and Environmental Issues

History of Industrial Revolution

Steam Engine

Coal
First Industrial Revolution
(18th~19th century)

Oil
Second Industrial Revolution
(End of the 19th century ~ Early 20th century)

Renewable energy
Third Industrial Revolution
(21st century ?)

Fossil energy economy
12 billion ton of oil equivalent

Sustainable economy
Hydrogen carrier

Fuel Cell

Internal Combustion Engine

1. Energy and Environmental Issues
Hydrogen Carriers (solid and liquid carriers)

Volumetric density

Packing ratio

Face-centered cubic structure

Hexagonal closed packed structure

Bulk density of Mg: 0.7g/cm³

Packing ratio: 74% (theoretical value)

Packing ratio: 40% (practical value)

Packing ratio(relative density): 40-50% (practical value)

2. Properties of Ammonia

Volumetric H₂ densities of hydrogen carriers

Liquefaction at room temperature and 1MPa

Volumetric H₂ density of liquid NH₃: (1.5) × H₂ density of liquid H₂

Volumetric H₂ density of ammonia: maximum value
Enthalpy difference (heat of formation) for hydrogen desorption

Heat of formation for \( \text{NH}_3 \) : about 10% of heat of combustion for \( \text{H}_2 \)
3. Safety of Ammonia

Ammonia concentration 100% (deleterious substance) $\rightarrow$ Hydrogen carrier

Flammability of hydrogen carrier

- MH
- Ti-Cr-V
- MgH$_2$
- MCH
- Toluene
- NH$_3$
- Liquid H$_2$
- Compressed H$_2$ (70MPa)
4. Production, Storage and Transportation of Ammonia

Ammonia production process (Haber-Bosch process)

- **Nitrogen from the air**
- **Hydrogen from natural gas**

**Reactor**
- 20MPa
- 400~500°C
- Iron catalyst

- **N₂ and H₂**
  - 1:3 by volume

- **Unreacted Gases Recycled**

- **Gases are cooled**

- **Liquid NH₃**

**CIF price of NH₃ in Japan:** 300-400 yen/kgH₂ ($3/kgH₂)

**Compressed H₂ price in Japan:** 1000-1100 yen/kgH₂ ($9/kgH₂)
Storage and Transportation of NH₃

World production: 1.8 hundred million ton/year (2013)

Transportation 30,000 tons level by tanker ship

MC331
11500gal, 300psi

900 fuel cell vehicles

Storage 15,000 tons level

Transportation 26tonns by trailer (H₂: 4.6tonns)

World production capacity: 2.1 hundred million ton/year (2013)

http://www.fao.org/3/a-i4324e.pdf
5. Ammonia Utilization as a Hydrogen Carrier

**Fuel cell vehicle vs. hybrid vehicle**

**MIRAI**
Price: around $60,000

- **H₂ price:** 1000-1100yen/kg ($9/kg)
- **Fuel consumption rate:** 135km/kg
- **Fuel price:** 7.4-8.1yen/km (¢6/km)

**Lexus GS 450h**
Price: around $60,000

- **Gasoline price:** 130-150yen/L ($1.1/L)
- **Fuel consumption rate:** 18.2km/L
- **Fuel price:** 7.1-8.2yen/km (¢6/km)

Scenario of Fuel Cell Commercialization Conference of Japan (FCCJ)
2 millions of FCV and construction of around 1,000 hydrogen stations in 2025
Volumetric $\text{H}_2$ density of ammonia: maximum, Enthalpy difference for $\text{H}_2$ desorption: small → Hydrogen station using $\text{NH}_3$: key issue


<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity of $\text{H}_2$</td>
<td>99.97%</td>
</tr>
<tr>
<td>Total hydrocarbons ($\text{C}_1$)</td>
<td>2ppm</td>
</tr>
<tr>
<td>Water ($\text{H}_2\text{O}$)</td>
<td>5ppm</td>
</tr>
<tr>
<td>Oxygen ($\text{O}_2$)</td>
<td>5ppm</td>
</tr>
<tr>
<td>$\text{N}_2$, $\text{Ar}$</td>
<td>100ppm</td>
</tr>
<tr>
<td>He</td>
<td>300ppm</td>
</tr>
<tr>
<td>Carbon Dioxide ($\text{CO}_2$)</td>
<td>2ppm</td>
</tr>
<tr>
<td>Carbon Monoxide ($\text{CO}$)</td>
<td>0.2ppm</td>
</tr>
<tr>
<td>Total sulphur compounds</td>
<td>0.004ppm</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.01ppm</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.2ppm</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1ppm</td>
</tr>
<tr>
<td>Total halogenated compounds</td>
<td>0.05ppm</td>
</tr>
</tbody>
</table>

**Fuel cell**

- Catalyst
- Proton exchange membrane
- $\text{O}_2$
- Water
- H$_2$

**Ammonia concentration below 0.1ppm**
Purpose of research and development

Ammonia decomposition and high purity H\textsubscript{2} supply system

\[ \text{NH}_3 \rightarrow (1/2)\text{N}_2 + (3/2)\text{H}_2 \]


NH₃ decomposition catalysts

Ammonia conversion at chemical equilibrium calculated by HSC chemistry

0.1MPa

NH₃ conversion >99.7%
NH₃: about 1000ppm

Ni-based catalysts
NH₃ conversion 20-60%
Ru-based catalysts using conventional oxide
NH₃ conversion 60-90%

Temperature /K

NH₃ conversion /%
Catalytic activity of Ru-based catalysts at 500°C

NH\textsubscript{3} absorbing materials

Plateau pressure of metal ammine chloride

<table>
<thead>
<tr>
<th>Material</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2}</td>
<td>0.0002MPa</td>
</tr>
<tr>
<td>Ca(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2}</td>
<td>0.03MPa</td>
</tr>
<tr>
<td>Li(NH\textsubscript{3})\textsubscript{4}Cl</td>
<td>0.18MPa</td>
</tr>
</tbody>
</table>

2000ppm (0.1MPa)
\[
\begin{align*}
\text{MgCl}_2 & \text{ absorbs ammonia to form 3 kinds of ammine complexes} \\
\text{MgCl}_2 + \text{NH}_3 & \rightarrow \text{Mg(NH}_3\text{)Cl}_2 \\
\text{Mg(NH}_3\text{)Cl}_2 + \text{NH}_3 & \rightarrow \text{Mg(NH}_3\text{)}_2\text{Cl}_2 \\
\text{Mg(NH}_3\text{)}_2\text{Cl}_2 + 4\text{NH}_3 & \rightarrow \text{Mg(NH}_3\text{)}_6\text{Cl}_2
\end{align*}
\]

\[
\begin{align*}
\text{Standard enthalpy change } & \Delta H^0 \\
\text{Standard entropy change } & \Delta S^0 \\
\text{-87 kJ/mol} & -135 \text{ J/molK} \\
\text{-75 kJ/mol} & -134 \text{ J/molK} \\
\text{-56 kJ/mol} & -135 \text{ J/molK}
\end{align*}
\]

\[
\begin{align*}
\text{Mg(NH}_3\text{)}_6\text{Cl}_2 & \text{ is formed at room temperature (PCI, XRD, TG-MS)} \\
\]

\[
\begin{align*}
\text{After activation of } \text{MgCl}_2, & \text{ Mg(NH}_3\text{)Cl}_2 \text{ is formed at high temperature of 230-300°C (PCI, XRD, TG-MS)}
\end{align*}
\]

\[
\begin{align*}
\text{van’t Hoff plot: accurate evaluation of } & \Delta H^0 \text{ and } \Delta S^0 \text{ for mono-ammine complex}
\end{align*}
\]

S. Lysgaard et al., Int. J. Hydrogen Energy, 37, 18927-18936 (2012)

T. Aoki et al., The Iron and Steel Institute of Japan and The Japan Institute of Metals and Materials, Chugoku Shikoku Branch National Meeting, August 19-20, Hiroshima, Japan 2015.
MgCl₂ + NH₃ → Mg(NH₃)Cl₂

Mono-ammine complex of MgCl₂
Revised standard enthalpy change -64 ± 1 J/mol NH₃
Revised standard entropy change -97 ± 2 J/mol K

Standard enthalpy change -87 kJ/mol NH₃
Standard entropy change -135 J/mol K

van’t Hoff plot for mono-ammine complex of MgCl₂

\[ \ln P_{eq} = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R} \]

Plateau pressure / Pa

NH₃: 1000 ppm → NH₃: 0.5 ppm (0.1 MPa)
Ammonium Hydrogen Sulfate

\[ \text{NH}_4\text{HSO}_4 + \text{NH}_3 \leftrightarrow (\text{NH}_4)_2\text{SO}_4 \]

Standard enthalpy change: \(-108\text{kJ/molNH}_3\)

Standard entropy change: \(-193\text{J/molK}\) (entropy of NH\(_3\): 193J/molK)

van’t Hoff plot for ammonium hydrogen sulfate-ammonia system

\[
\ln P_{eq} = \frac{\Delta H^0}{RT} - \frac{\Delta S^0}{R}
\]

\(\text{NH}_3:1000\text{ppm} \rightarrow \text{NH}_3: \text{below 0.1 ppm (0.1MPa)}\)

\(\text{Below 0.01Pa}\)

\(20^\circ\text{C}\)
A small amount of NH$_3$ determination method

Break through testing apparatus

(FTIR - Gas Cell) Optical path length: 1.5m

0.1-1000 ppm (0.1 MPa)

Hydrogen/ammonia mixed gas around 0.1 MPa (NH$_3$: 1000 ppm)

Breakthrough curve for ammonia absorption from H₂/NH₃ in ammonium hydrogen sulfate by FTIR - Gas Cell

Hydrogen/ ammonia mixed gas at 0.15MPa (NH₃: 1000ppm), 100cc/min

NH₃: below 0.1ppm (0.1MPa), 9.2wt%[(NH₄)₂SO₄]
Conceptive picture of H\textsubscript{2} station using NH\textsubscript{3}

Ammonia decomposition and high purity H\textsubscript{2} supply system

NH\textsubscript{3} \rightarrow \text{Compressor} \rightarrow \text{Accumulator} \rightarrow \text{Dispenser}

\text{H}_2 \text{O} \rightarrow N_2

Air contains 80\% nitrogen.
6. Summary

1. Ammonia is a hydrogen carrier having maximum volumetric H$_2$ density of about 11kgH$_2$/100L.

2. Heat of formation for NH$_3$ is about 10% of heat of combustion for H$_2$.

3. Ammonia can transport 4.6 tons of hydrogen by trailer, which corresponds to 900 fuel cell vehicles.

4. High purity hydrogen gas will be produced by Ru-based catalyst, ammonia absorption materials.
Acknowledgement

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WHTC 2019
Tokyo, Japan
8th World Hydrogen Technologies Convention
June 2(Sunday)-7(Friday), Tokyo International Forum

All Japan governmental, industrial and academic sectors will provide exhibition and forum for the latest hydrogen technology.

Chair Y. Kojima, Co-Chair H. Takagi

Thank you for your attention.

Hosted by WHTC 2019 Organizing Committee
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