Liquid Ammonia for Hydrogen Storage

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Hiroshima Peace Memorial
Itsukushima Shinto Shrine
Peace Memorial City
1. Energy and Environmental Issues

Energy and Environmental Issues  Renewable energy

Solar energy
(50 times of Annual global energy consumption by humans)

Solar thermal

Wind

Geothermal

Hydro

Tidal power

Wave power

Solar cell

Electric power

Hydrogen (gas) → Hydrogen carrier (solid, liquid)
2. Research on hydrogen carrier (hydrogen storage materials) and systems (1999~2014)

Inorganic hydrides (thermolysis)

- MgH₂
- NH₃BH₃
- LiBH₄
- LiNH₂
- Ti-Cr-Mn(AB₂)
- Ti-Cr-V(BCC)

Organic hydrides

- Methylcyclohexane ⇔ Toluene

Hydrogen absorbing alloys

Carbon materials (77K)

Thermolysis of inorganic hydrides

Control heat of formation and kinetics

Mg-based nano-composite material ($\text{Nb}_2\text{O}_5:1\text{mol}$%)

$\text{LiH-NH}_3$

$\text{NaH-NH}_3\text{BH}_3$

2$\text{LiBH}_4-\text{MgH}_2$

NANO-COMPOSITE MATERIALS

1. Catalyst
   - Kinetics
   - Catalyst
   - Hydrogen storage materials

2. Composite Hydrides
   - Thermodynamics
   - $\Delta H$
   - $\Delta S$

3. Nano-crystallites
   - Kinetics, Thermodynamics
   - Catalyst
   - Hydride
   - $\text{Li-N-H}$

- Catalyst
- Hydride ($\text{H}^{\delta}$+)
- Hydride ($\text{H}^{\delta}$-)
- 10 nm

Packing densities of solid-state hydrides with light elements

Face-centered cubic structure

Packing ratio: 74% (theoretical value)

Packing ratio: 50% (practical value)

Volumetric H₂ density: below 8kgH₂/100L
3. Properties and Safety of Ammonia

H₂ densities of hydrogen carrier (solid, liquid)

Volumetric H₂ density of liquid NH₃: (1.5-2.5)×H₂ density of liquid H₂

[Graph showing various hydrogen storage materials and their densities]

NH₃: burnable substance → Energy carrier
Ammonia tank

10mass%, 8.2kgH₂/100L

High pressure H₂ tank (70MPa)

5mass%, 2.8kgH₂/100L

High-pressure MH tank (Ti-Cr-Mn + compressed H₂)

Hydrogen generator using sodium borohydride

Reactor, catalyst, separator, pump

1.7mass%, 4.1kgH₂/100L

Metal Hydride (Ti₁₁CrMn)

2.0mass%, 1.5kgH₂/100L

Filter

Fin

Fueltank (25L) NaBH₄

Byproduct tank (25L) NaBO₂

130mm

150 mm
Heat of formation and H₂ storage capacity

LaNi₅

Heat of formation for NH₃: about 10% of heat of combustion for H₂
# Costs of NH₃ and H₂

<table>
<thead>
<tr>
<th>Item</th>
<th>NH₃</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price in Japan (Yen/Nm³H₂)</td>
<td>27-36(2013)</td>
<td>122</td>
</tr>
<tr>
<td>Production cost ($/kgH₂) 2200ton/day USA</td>
<td>3.80</td>
<td>3.00</td>
</tr>
<tr>
<td>Transportation cost ($/kgH₂) 1610km Pipe line USA</td>
<td>0.19</td>
<td>0.51-3.22 (1.87)</td>
</tr>
<tr>
<td>Storage cost ($/kgH₂) 15 day USA</td>
<td>0.06</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>182 day USA</td>
<td>0.54</td>
</tr>
<tr>
<td>Supply cost ($/kgH₂) USA</td>
<td>4.05-4.53</td>
<td>5.5-21</td>
</tr>
</tbody>
</table>

Cost of NH₃ in Japan: 20-30% of cost of H₂
Safety

Industrial accidents involving ammonia and hydrogen

Australia (1920-), Canada (1917-), China (1978-), France (1905-), Germany (1900-), India (1944-), Italy (1907-), Japan (1922-), Mexico (1950-), Netherlands (1807-), Russia (1992-), Spain (1958-), Sweden (1864-), UK (1879-), USA (1873-)

Hazardous substance
Controlled fuel

Distribution amount
NH₃ : 150 million tonnes / year
H₂ : 4 million tonnes / year

The number of accidents

Incidents  Fatal

http://www.elucidare.co.uk/news/Ammonia%20as%20H2%20carrier.pdf
Ammonia absorbing materials using borohydrides and metal halides

P-C isotherm for NaBH₄-NH₃ system (amine complex)

NH₃ vapor pressure of NaBH₄ < NH₃ vapor pressure

Safer ammonia

Plateau pressure of lithium ammine halide

Electronegativity difference ($\chi_p$) for LiBr, LiCl, and LiF with respective plateau pressures.

- LiBr: 1.98, <0.001 MPa
- LiCl: 2.18, <0.001 MPa
- LiF: 3, >0.8 MPa

The smaller the electronegativity difference is, the lower plateau pressure is achieved. Safety improvement.
Plateau pressure vs electronegativity difference

Ammonia pressure /MPa

Electronegativity difference ($\chi_p$)

$\chi_p = 2.2$

Ammonia absorption: $\chi_p < 2.2$
4. Hydrogen Economy Using Ammonia

**NH₃ production using solar heat**

Solar concentrating system (trough)

**H₂ production using solar heat**

NH₃ production

NH₃ delivery

Energy stock

Hydrogen production plant

**Heat storage**

NH₃ utilization

Large-scale moving vehicle

CO₂: 0

NH₃ fuel

NH₃ power plant, SOFC

H₂ → NH₃

Domestic use fuel cell

NH₃ delivery

Small scale NH₃ production
Conceptive picture of ammonia energy system

**NH₃ production**
Power to Liquid (PTL)

**Solar heat**
24h

**NH₃ utilization**

```
NH₃ + 0.08O₂ → 0.5N₂ + 0.16H₂O + H₂
```

```
NH₃ + 0.75O₂ → 0.5N₂ + 1.5H₂O
```

**Energy output**

**Storage - transportation**

Concise conversion equations:

- NH₃ + 0.08O₂ → 0.5N₂ + 0.16H₂O + H₂
- NH₃ + 0.75O₂ → 0.5N₂ + 1.5H₂O
4.1 \( \text{NH}_3 \) production

Direct thermal decomposition of water
(Hydrogen yield calculated by HSC Chemistry 6.0)

![Graph showing hydrogen yield vs. temperature](image)

- Yield: 64% at 4000°C
- Below 650°C

Thermochemical water splitting, Steam-electrolysis
The possibility of H₂ production below 500 °C by water-splitting via reactions of the Na Redox system was experimentally demonstrated.
Entropy ($\Delta S$) control

Na metal

2Na$_2$O $\rightarrow$ Na$_2$O$_2$ + 2Na(g)  $\text{500}\,^\circ\text{C}$

Na$_2$O$_2$ + H$_2$O(l) $\rightarrow$ 2NaOH + 1/2O$_2$  $\text{100}\,^\circ\text{C}$

2NaOH + 2Na(l) $\rightarrow$ 2Na$_2$O + H$_2$  $\text{350}\,^\circ\text{C}$

Haber-Bosch process
4.2 NH₃ utilization

Toyota will sell in California the summer of 2015, Price: around $70,000.

Driving range: 700km
Filling time: 3 minutes
140-160km/kgH₂

Honda will sell in 2015
Price: $70,000 - $80,000

Driving range: 800km
Filling time: 3 minutes

Hydrogen price: barrier to the popularization

NH₃ decomposition and removal technology to produce H₂
NH₃ decomposition technology

Catalytic activity

<table>
<thead>
<tr>
<th>Cartalyst</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>673K</td>
</tr>
<tr>
<td>Ru/CNT-KNO₃</td>
<td>50</td>
</tr>
<tr>
<td>Ru-KNO₃/MgO-CNTs</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>30000 mLg⁻¹h⁻¹</td>
</tr>
<tr>
<td>Ru/LSZ-DP</td>
<td>18</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>5</td>
</tr>
<tr>
<td>Ni/La₂O₃</td>
<td>6</td>
</tr>
<tr>
<td>Fe₂O₃/CMK-5</td>
<td>9(723)</td>
</tr>
<tr>
<td>NiO/Al₂O₃</td>
<td>6(723)</td>
</tr>
<tr>
<td>Nano-Ni/Zeolite(1h)</td>
<td>–</td>
</tr>
<tr>
<td>Nano-Ni/Zeolite(1h)</td>
<td>–</td>
</tr>
</tbody>
</table>

ISO14687-2

Ammonia concentration: <0.1ppm

1. Alkali metal hydride-NH₃ system (reaction)
2. Metal ammine complex (absorption)
3. Adsorbent
4. Separation membrane

LSZ: Lanthanum-stabilized zirconia, CMK-5: Ordered mesoporous carbon
Outline
Promote the realization of a hydrogen-oriented society through research on efficient and low-cost hydrogen production technology, liquid hydrogen for efficient transport and storage, and energy carrier technology

NH₃ production and utilization technologies

Japan Science and Technology (JST) Strategic Basic Research Program Advanced Low Carbon Technology Research and Development Program Special Priority Research Areas Energy Carrier, July 2013-2014

SIP (Cross-ministerial Strategic Innovation Promotion Program) “Energy carrier” (Council for Science, Technology and Innovation of the Cabinet Office). 2014-

Program Director (Cabinet Office)
Shigeru Muraki
(Director and Vice Chairman of the Board of Tokyo Gas Co., Ltd.)
1. We have evaluated 200 kinds of hydrogen storage materials (hydrogen absorbing alloys, inorganic materials, carbon materials).

2. Liquid Ammonia has been expected as a hydrogen energy carrier because it has a high H₂ storage capacity with 17.8 mass% and the volumetric hydrogen density is 1.5-2.5 times of liquid hydrogen.

3. Ammonia has advantages in cost and convenience as a renewable liquid fuel for fuel cell vehicles, SOFC, electric power plants, air crafts, ships, and trucks.

4. Power to liquid ammonia (PTL) is a promising technology to establish hydrogen economy.
Tokyo has been chosen to host the World Hydrogen Technologies Convention (WHTC) 2019.

WHTC Venue History
1st 2005 Singapore
2nd 2007 Montecatini Terme
3rd 2009 Delhi, India
4th 2011 Glasgow, UK
5th 2013 Shanghai, China
6th 2015 Sydney, Australia
7th 2017 Prague, Czech
8th 2019 Tokyo, Japan

Thank you for your attention.

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