NH₃ as a Hydrogen Career

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1. Energy and Environmental Issues

**History of Industrial Revolution**

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

- **Oil (Natural gas)**
  - 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**

- Secondary energy → H₂
2. Research on Hydrogen Storage Materials

Hydrogen career?

↓

Liquid hydrogen

Liquid hydrogen (20K), 7kgH₂/100L

3.7 billion ton/year

Liquefying the hydrogen uses 30-40% of the hydrogen’s energy content
Development of FCV (2000 ~)

Honda FCX (35MPa)  Toyota FCHV (70MPa)

Cruising distance: 620km,  Cruising distance: 830km

Internal volume: 171L, 3.9kgH₂  Internal volume: 156L, 6.1kgH₂

130-160km/1kgH₂

Toyota aims for $50,000 production hydrogen sedan by 2015

Hydrogen storage materials
Hydrogen storage materials (1999 ~ 2012)

Evaluation and characterization of 200 kinds of hydrogen storage materials

Hydrogen absorbing alloy
Complex hydrides
Inorganic hydrides
Porous materials

Organic hydrides

CH₃

CH₃

CH₃
Gravimetric and volumetric H$_2$ densities of hydrogen storage materials

Volumetric H$_2$ density in NH$_3$: 1.5×liquid H$_2$

Maximum volumetric H$_2$ density

Gravimetric and volumetric H$_2$ densities of hydrogen storage materials

- Hydride (calculated value)
- H$_2$ storage materials (experimental value)
- High pressure tank of 70MPa

Liquid H$_2$
3. Characteristics of NH₃

Haber-Bosch process
10-25MPa, 573-823K
N₂ + 3H₂ → 2NH₃
Annual production of the world 153 million ton (2008)

California farmer, Injection of liquid ammonia in a sugar beet field

NH₃: Inclusion of hydrogen

Renewable fuel independent of fossil fuel
**NH₃**
0.18kgH₂/kg material
0.107kgH₂/L material

DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity:</td>
<td>kWh/kg (kg H₂/kg system)</td>
<td>1.5 (0.045)</td>
<td>1.8 (0.055)</td>
<td>2.5 (0.075)</td>
</tr>
<tr>
<td>Usable, specific-energy from H₂ (net useful energy/max system mass)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System Volumetric Capacity:</td>
<td>kWh/L (kg H₂/L system)</td>
<td>0.9 (0.028)</td>
<td>1.3 (0.040)</td>
<td>2.3 (0.070)</td>
</tr>
<tr>
<td>Usable energy density from H₂ (net useful energy/max system volume)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Storage System Cost b:</td>
<td>$/kWh net ($/kg H₂)</td>
<td>TBD (TBD)</td>
<td>TBD (TBD)</td>
<td>TBD (TBD)</td>
</tr>
<tr>
<td>Fuel cost c</td>
<td>$/gge at pump</td>
<td>3-7</td>
<td>2-4</td>
<td>2-4</td>
</tr>
</tbody>
</table>

$2-4/gge (2010 ~ 2011)

Gasoline gallon equivalent
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Mg(BH₄)₂</th>
<th>NH₃</th>
<th>H₂ absorbing alloy (LaNi₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ content ΔH</td>
<td>15mass%</td>
<td>18mass%</td>
<td>1.5mass%</td>
</tr>
<tr>
<td>H/M: 2, H₂:11mass%</td>
<td>-57 ~ -75kJ/molH₂</td>
<td>-31kJ/molH₂</td>
<td>-31kJ/molH₂</td>
</tr>
<tr>
<td>ΔH: -285kJ/molH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H/M: 3, H₂:18mass%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔH: -31kJ/molH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Stable under water and oxygen
From above it is seen that ammonia is the most hazardous due to health effects, but the least hazardous due to flammability. All considered substance /compounds are ranked as not reactive in emergency situations.

Safety number: Ammonia=Hydrogen
4. NH₃ utilization

Energy carrier

4NH₃ → 2N₂ + 6H₂

6H₂ + 3O₂ → 6H₂O

Hydrogen carrier

4NH₃ → 2N₂ + 6H₂

6H₂ + 3O₂ → 6H₂O

NH₃

Energy carrier

Gas turbine

SOFC

ICE vehicle

Hydrogen carrier

FCV

Domestic fuel
### 4.1 Large scale power generation using gas turbine (Output power: Million kW, 1000MW)

#### Preliminary calculation of energy balance (WE-NET: 1996)

<table>
<thead>
<tr>
<th>Item</th>
<th>Liquid H₂ system</th>
<th>NH₃ system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input electric energy</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Energy after production</td>
<td>72.9</td>
<td>70.3</td>
</tr>
<tr>
<td>Energy loss by transportation (5000km)</td>
<td>(2.5)</td>
<td>(1.6)</td>
</tr>
<tr>
<td>Energy after transportation</td>
<td>70.4</td>
<td>68.7</td>
</tr>
<tr>
<td>Plant cost /million dollars</td>
<td>7400</td>
<td>5400</td>
</tr>
</tbody>
</table>

#### Energy generated (Efficiency: 60%)

- **Hydrogen carrier**
  - *Combined Cycle*
  - **42** H₂ gas turbine (100-300MW)
- **NH₃ carrier**
  - **32** H₂ gas turbine
  - **41** NH₃ gas turbine

4.2 Next generation vehicle development

Fuel consumption of next generation vehicle

Without emission of CO₂

Fuel consumption
/km/kWh

<table>
<thead>
<tr>
<th>Vehicle Type</th>
<th>Fuel Consumption</th>
<th>Distance</th>
<th>Weight</th>
<th>Pressure</th>
<th>Capacity</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline Vehicle</td>
<td>4.2 km/kWh</td>
<td>1700km</td>
<td>1310kg</td>
<td>70MPa</td>
<td>156L</td>
<td>30-40%</td>
</tr>
<tr>
<td>Hybrid Vehicle</td>
<td>8.3 km/kWh</td>
<td>830km</td>
<td>1880kg</td>
<td>1MPa</td>
<td>88L</td>
<td>60%</td>
</tr>
<tr>
<td>EV</td>
<td>1.7 km/kWh</td>
<td>790km</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCV</td>
<td>0.6 km/kWh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃ hybrid Vehicle</td>
<td>1.8 km/kWh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculation

Fuel consumption $\propto$ Tank to wheel $\propto$ efficiency

Ammonia is both caustic and hazardous

Hybrid-truck (controlled fuel)
4.3 Energy and hydrogen career

Ammonia storage issue (Energy and hydrogen careers for gas turbine, SOFC, ICE vehicle FCV)

1. High flash point, High Decomposition temperature (above 400°C)
2. Toxic to humans

Research purposes

1. Conversion from ammonia to hydrogen (mixture of H₂ and NH₃, generation of high purity H₂), Cold start
2. Ammonia storage materials (lower vapor pressure), Harmless NH₃
(1) Conversion from ammonia to hydrogen at RT

$\text{LiH} + \text{NH}_3 \rightarrow \text{LiNH}_2 + \text{H}_2$ \hspace{1cm} (1)

$\Delta H^0: -43 \text{kJ/mol}$

$\text{H}_2$ generation at room temperature

MH-NH$_3$ 523-573K, 0.5MPa, H$_2$ flow


Molecular dynamics simulation

Hydrogen desorption curves of LiH-NH$_3$ system (room temperature)

A. Yamane, F. Shimojo, K. Hoshino, T. Ichikawa, Y. Kojima
Conversion system between NH$_3$ and H$_2$

NH$_3$ + LiH $\leftrightarrow$ LiNH$_2$ + H$_2$

0.1-0.6 MPa

Pressure gauge 1

Pressure Gauge 2

densitometer

Gas sampler

Reaction cell

Gas circulation pump

100-900 rpm

NH$_3$ Flow meter

NH$_3$ flow rate $\sim$ 50 cc/min (0°C, 1 atm)

Heater

50-400°C

0.5 g

Hydride

Collaborative research with Toyota Industries
Electrolysis of NH₃

ΔG₀: Standard Gibbs free energy difference = 13.1 kJ/mol

n = 3: Electron number responsible for reaction

E : Theoretical decomposition voltage

E(H₂O) = 1.23 V → E(NH₃) ?

\[ E = - \frac{\Delta G^0}{3F} + RT \ln(pN_2^{1/2}pH_2^{3/2})/nF \]

Vapor Pressure of NH₃ (25 °C)

0.5 V (experimental)

E(NH₃) = 0.038 V + 0.039 V = 0.077 V (theory)

We have detected hydrogen and nitrogen gas when SrTiO₃ and BaTiO₃ powder is mechanically milled under ammonia gas at room temperature.

(2) NH₃ absorbing materials

P-C isotherm for CaCl₂-NH₃ system

Vapor pressure of NH₃ at 19°C

NH₃ pressure /MPa

0.8
0.6
0.4
0.2
0

NH₃/CaCl₂ /mol/mol

0 2 4 6 8

0.06MPa

69-63kJ/mol 42kJ/mol 41kJ/mol

115g/L 107g/L

102kg 56kg

Ca(NH₃)₈Cl₂ Liquid NH₃

Rasmus Z. Sørensen et al., J. AM. CHEM. SOC. 130, 8660 (2008)
*Ab initio* molecular-dynamics (MD) simulation based on density functional theory (DFT).

Lower vapor pressure

Absorption energy

M > C > Li > N > K
5. Future perspective

H₂ production

H₂O → N₂ + 2H

NH₃ production

NH₃ utilization

NH₃ power plant
SOFC

Liq. NH₃

9000 km

Energy stock

Controlled fuel

Passenger car

Truck

Passenger car

9000 km

NH₃ Station
Realization of sustainable economy
( renewable energy economy )
( 2030 )

Best mix of NH₃, H₂ and electricity

NH₃  Controlled fuel

H₂

Secondary energy

Electricity
1. Ammonia has advantages in cost and convenience as a fuel for vehicle, electric power plant and SOFC.
2. LiH-NH\(_3\) system with TiCl\(_3\) desorbed 6 mass\% of H\(_2\) at room temperature.
3. Hydrogen gas was generated by the electrolysis of liquid ammonia.
4. We have detected hydrogen and nitrogen gas when SrTiO\(_3\) and BaTiO\(_3\) powder is mechanically milled under ammonia gas.
5. The vapor pressure of ammonia was decreased in metal chlorides.

**NH\(_3\) economy is a practical H\(_2\) economy**
September 21, 2012

Ministry of Education, Culture, Sports, Science and Technology (MEXT)
Ministry of Economy, Trade and Industry (METI)

$20 million
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Emerging Fuels (DOE)  Alternative Fuels ?

http://www.afdc.energy.gov/afdc/fuels/emerging.html
Thank you for your attention.