ALCA Advanced Low Carbon Technology Research and Development Program

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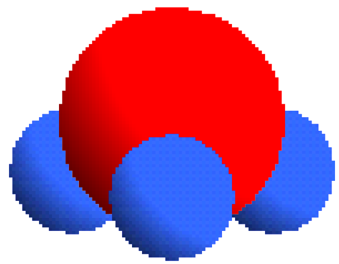
# A Green Ammonia Economy



## 22-25 of September 2013

## 10th Annual $NH_3$ Fuel Conference


## Yoshitsugu Kojima

## Hiroshima University

## Institute for Advanced Materials Research

# Table of Contents




Itsukushima Shinto Shrine

Hiroshima Peace Memorial

**Peace Memorial City**

# 1. Energy and Environmental Issues

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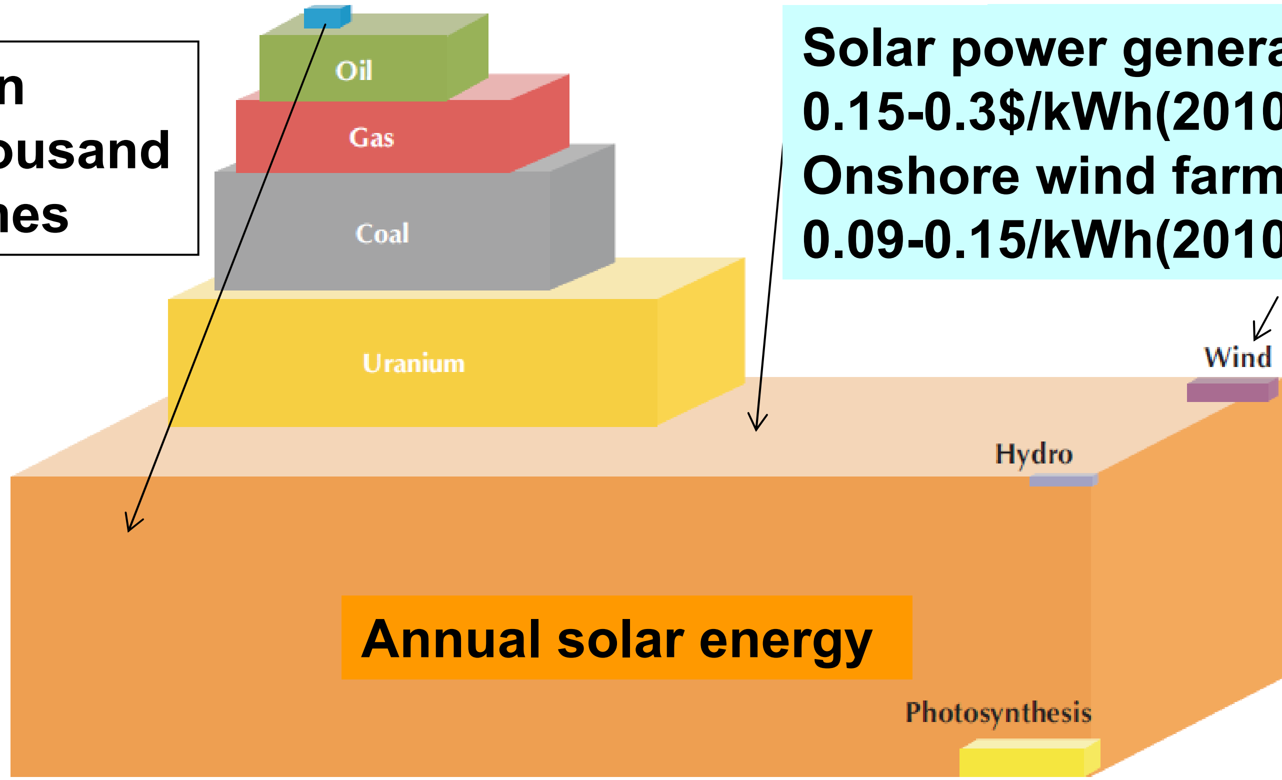
## Sustainable economy using renewable energy

**Annual global energy consumption by humans, oil, gas, coal, uranium reserves and annual solar energy**

Annual global energy consumption by humans

Ten thousand times



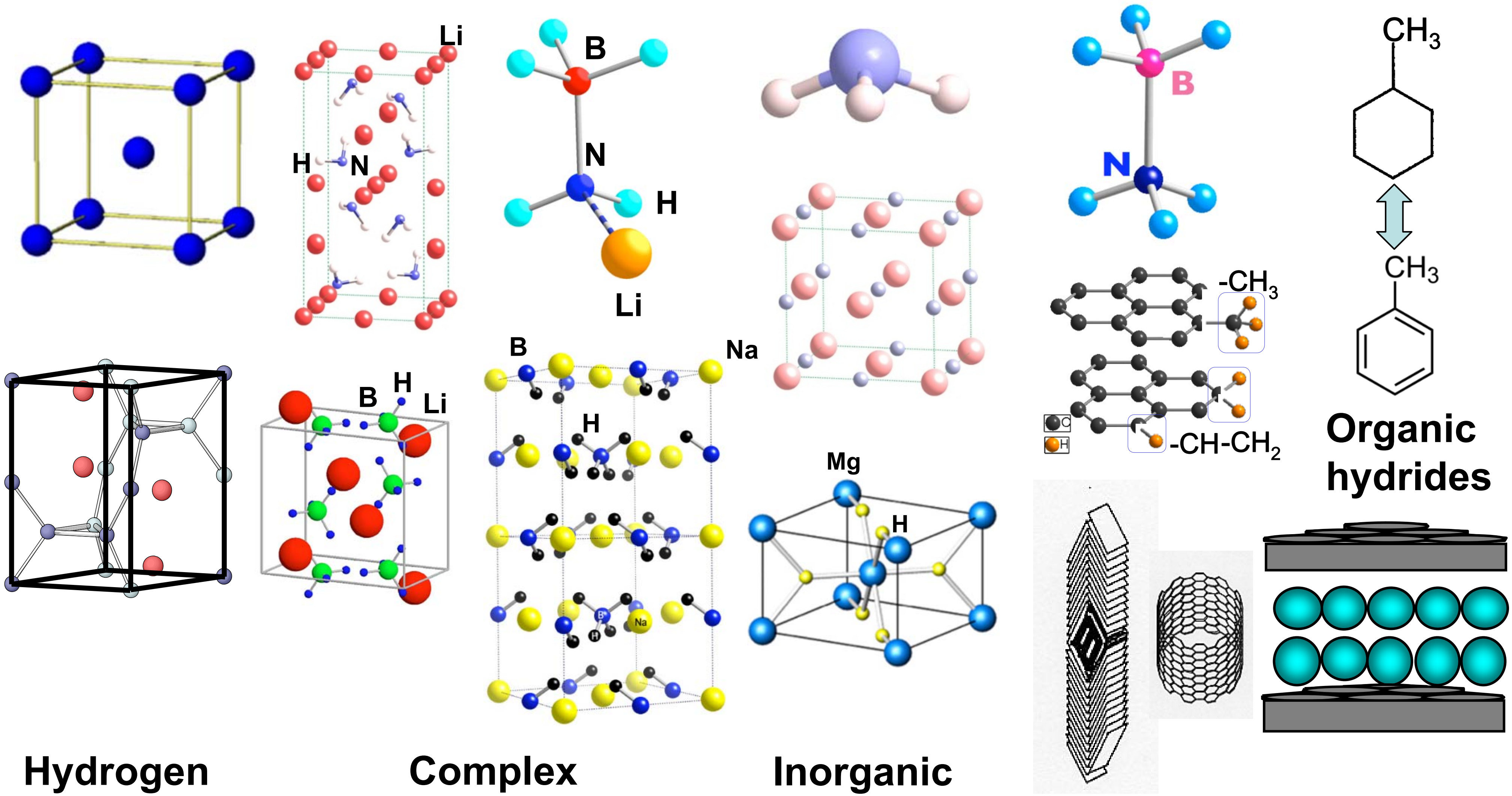

Source: National Petroleum Council, 2007, after Craig, Cunningham and Saigo (republished from IEA, 2008b).

Solar power generation,
0.15-0.3$/kWh(2010),0.05-0.07$/kWh(2030)
Onshore wind farms
0.09-0.15/kWh(2010), 0.05-0.08$/kWh(2030)

Electric power

Electric power → Energy career for renewable energy

# 2. Research on Hydrogen Storage Materials and Systems




Organic hydrides

Hydrogen absorbing alloy

Complex hydrides

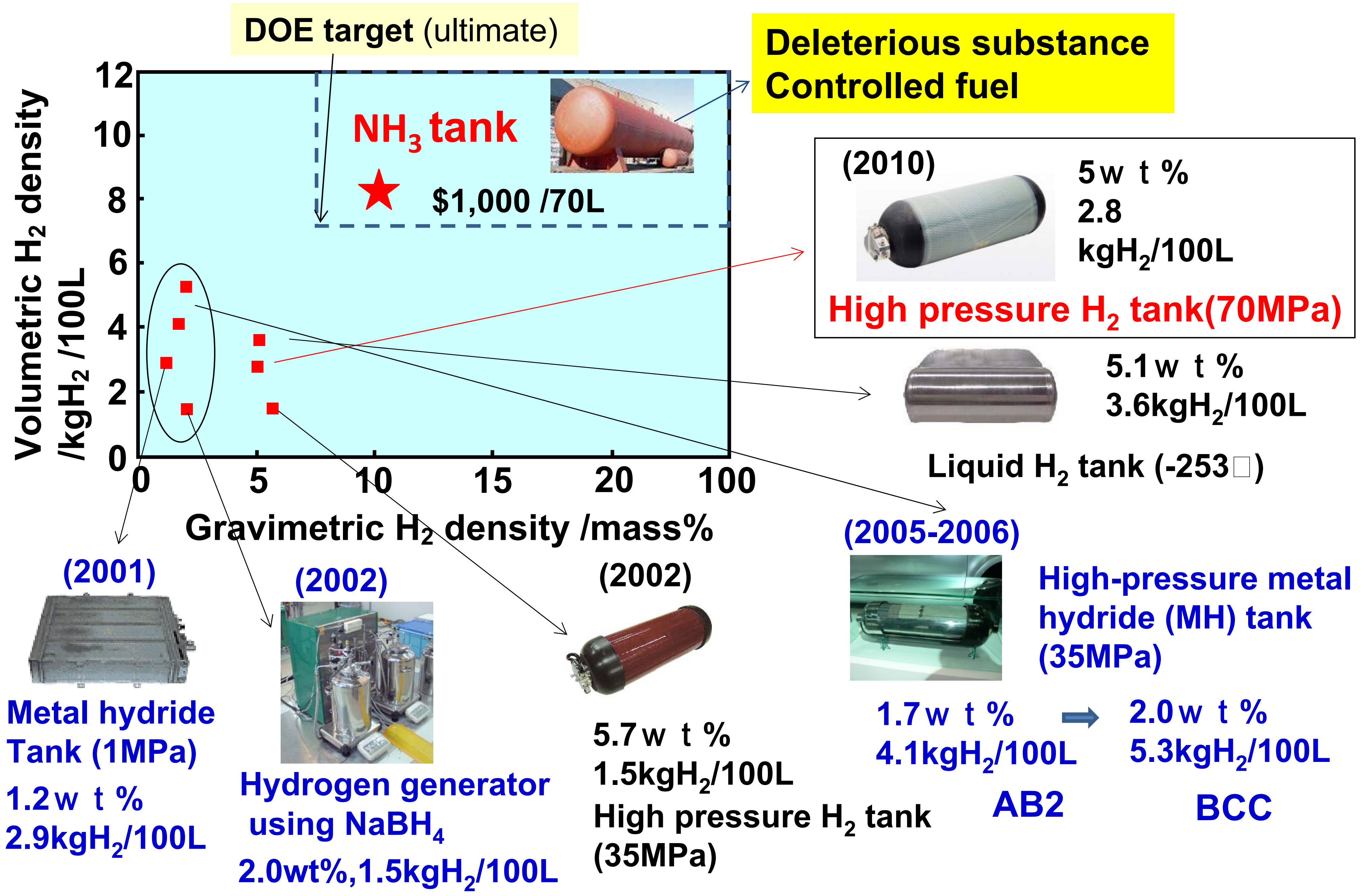
Inorganic hydrides

Carbon materials

**Evaluation and characterization of 200 kinds of hydrogen storage materials**

**Ammonia: Maximum volumetric $H_2$ density**

# Gravimetric and volumetric $H_2$ densities of hydrogen storage systems



# 3. Properties and Safety of Ammonia



## Volumetric $H_2$ densities of Liquid $NH_3$ and $H_2$

| Liquid $H_2$<br>Pressure, temperature | Liquid $NH_3$<br>Pressure, temperature | $H_2$ density of $NH_3$ /$H_2$ density of $H_2$ |
|---|---|---|
| 0.1MPa, -253□ | 1MPa, 25□ | 1.5 times |
| 0.1MPa, -253□ | 0.1MPa, -33□ | 1.7 times |
| 1MPa, -242□ | 1MPa, 25□ | 2.2 times |

**Volumetric $H_2$ density of liquid $NH_3$:**
**(1.5-2.2)×$H_2$ density of liquid $H_2$**

# Properties and costs of $NH_3$ and $H_2$

| Item | | $NH_3$ | | Hydrogen |
|---|---|---|---|---|
| Gravimetric $H_2$ density(wt%) | | 17.8 | | 100 |
| Volumetric $H_2$ density(kg/100L)<br>0.1MPa, -33□ (1MPa, 25□) | | 12.1(10.7) | > | 0.010(0.082) |
| Production cost($/kg$H_2$)<br>2200ton/day | | 3.80 | | 3.00 |
| Transportation cost($/kg$H_2$) | 1610km<br>パイプライン | 0.19 | | 0.51-3.22<br>(1.87) |
| Storage cost ($/kg$H_2$) $H_2$2664ton | 15 day | 0.06 | | 1.97 |
| | 182 day | 0.54 | | 14.95 |
| Supply cost($/kg$H_2$) | | 4.05-4.53 | < | 5.5-21 |

**Volumetric $H_2$ density in $NH_3$ at the same pressure and temperature : 100-1000 times**

# Safety of Ammonia(flammability)

## Flammability of Ammonia

| Substance | Flammable limits | Flash point | Ignition point |
|---|---|---|---|
| Ammonia GWP: 0 | 16-25% | 132□ | 651□ |
| Methane GWP: 21 | 5-15% | -188□ | 537□ |
| Hydrogen GWP: 0 | 4-74% | -157□ | 530□ |
| LPG(propane) | 2.1-9.5% | -104□ | 450□ |
| Methanol | 6-36% | 11□ | 464□ |
| Gasoline | 1.4-7.6% | -40□ | 300□ |

Editor-in-Chief David R. Ride, CRC Handbook of Chemistry and Physics 2008-2009 89th edition CRC Press, Taylor & Francis Group, Boca Raton, London, New York, http://www.jaish.gr.jp/anzen/gmsds/7664-41-7.html, http://www.toyokokagaku.co.jp/product/01_02_51.html, http://www6.nsk.ne.jp/toyama-kak/1hoanjoho/MSDSshu/MSDS/04.pdf,

**GWP: Global warming potential**

**From above it is seen that ammonia is the least hazardous due to flammability.**

# (Toxicity)

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## American Conference of Industrial Hygienists (ACGIH): 25ppm

**Medicine for insect bites**


minor aches, pains of muscles

Ammonia (2.3%)
21□(70F), Ammonia
Vapor pressure
0.003MPa

**Stimulant**


Ammonia (9.5-10.5%)
21□(70F), Ammonia
Vapor pressure
0.011MPa

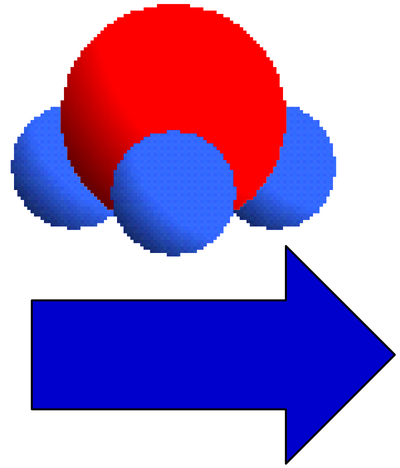
**Household Ammonia (Cleaner)**



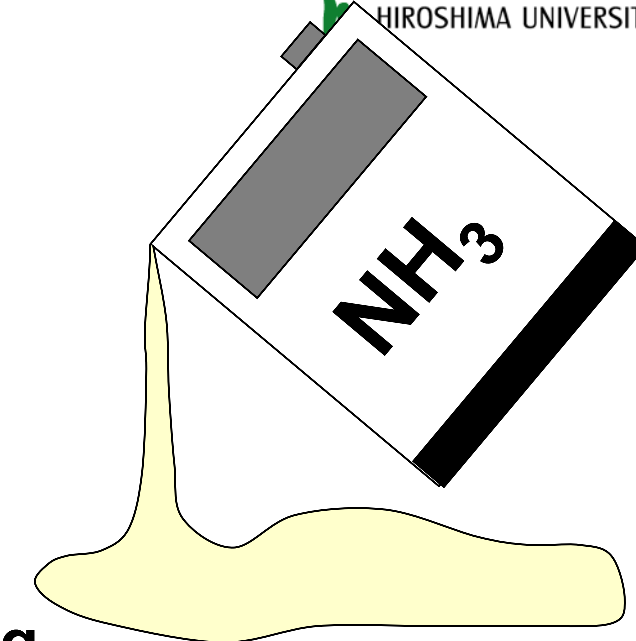

Ammonia (5-10%)
21□(70F), Ammonia
Vapor pressure
0.006-0.011MPa

**Familiar material**


**Fertilizer**



**Game-changing technology**




**Energy career**

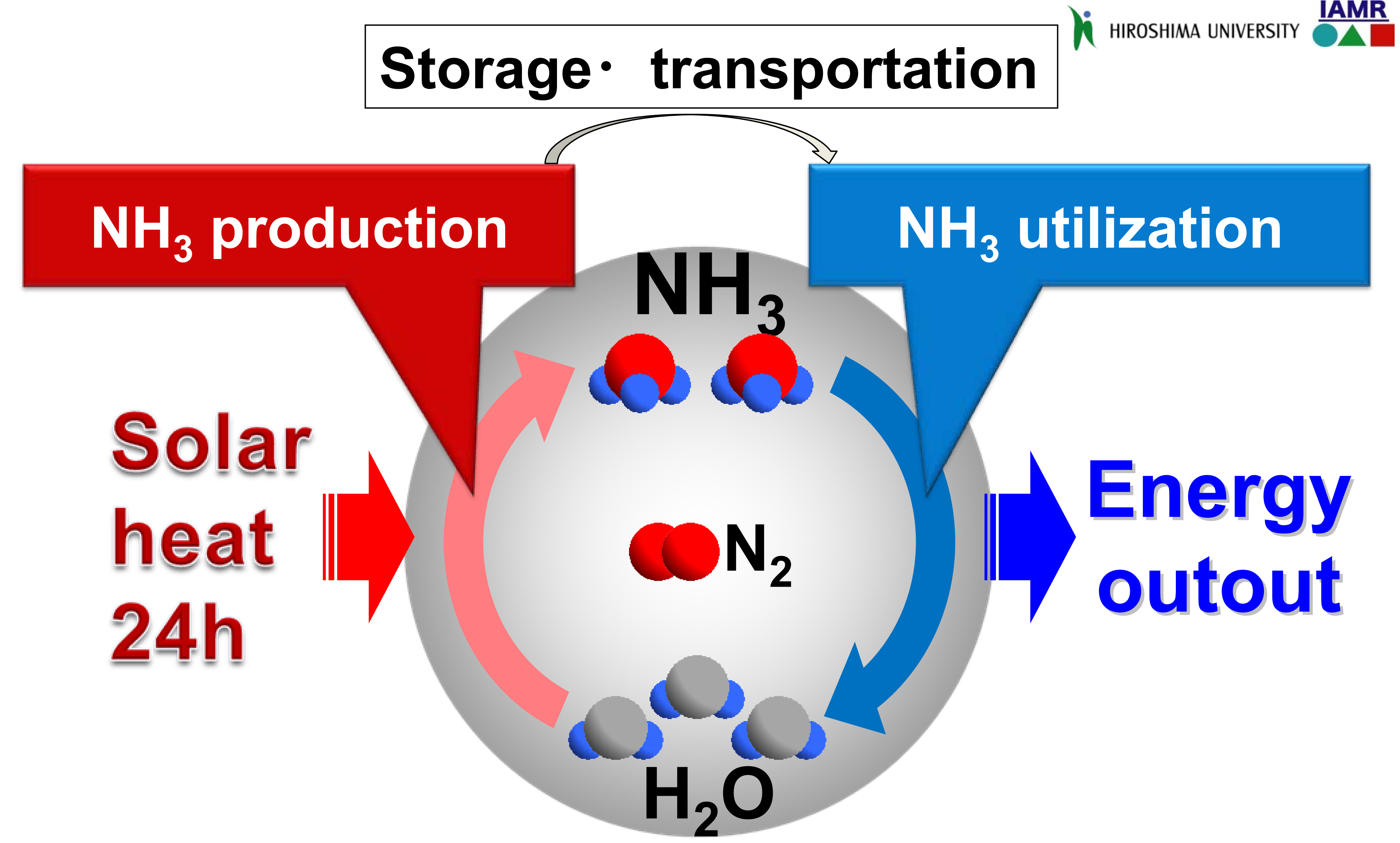
**Methane steam reforming: hydrogen**

**Haber-Bosch process**

**20-40MPa, 573-823K**

$$N_2 + 3H_2 \rightarrow 2NH_3$$

**Annual production of the world 198 million ton (2012)**




Conceptive picture of ammonia energy system

# 4. A Green Ammonia Economy

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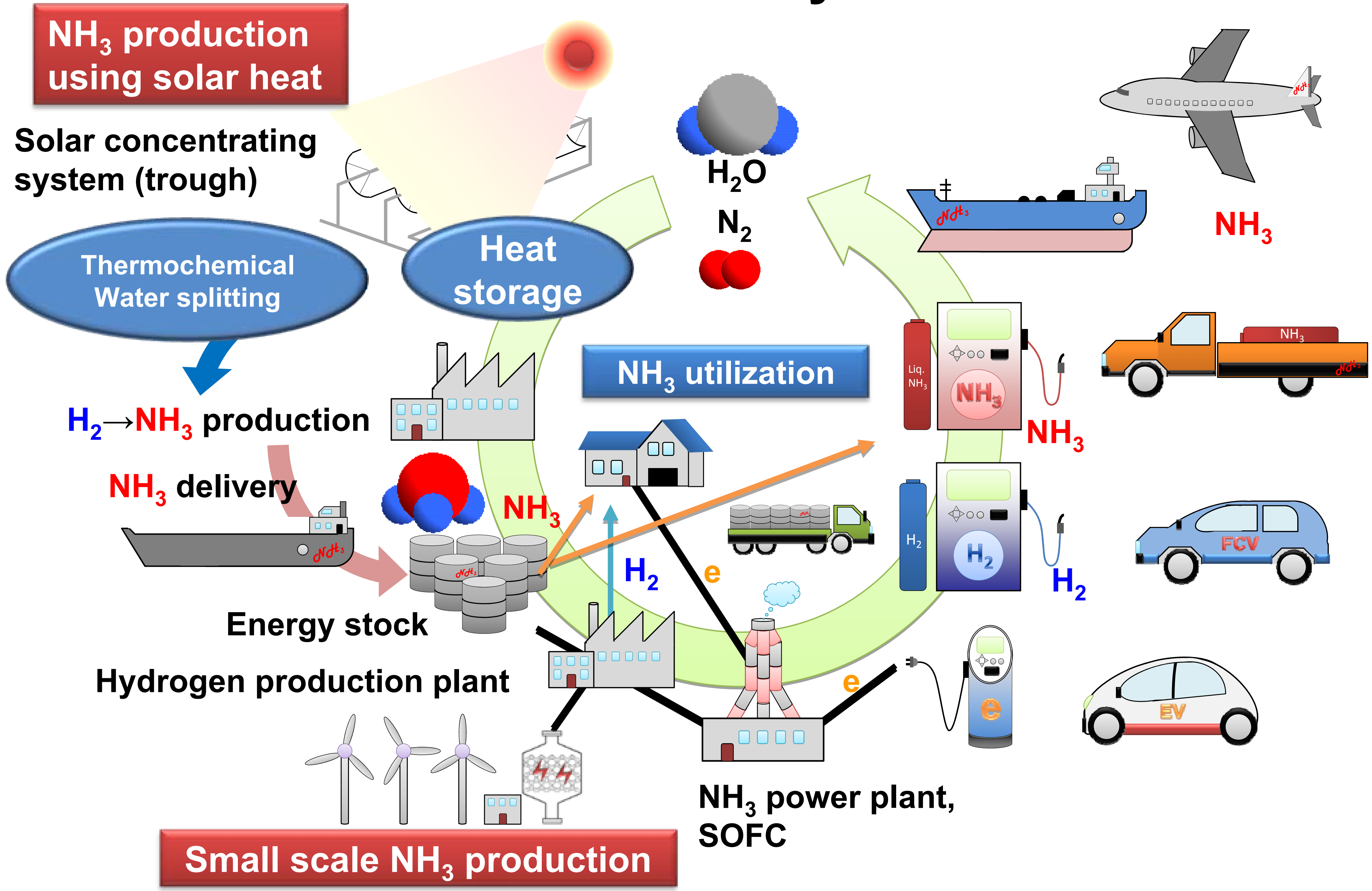
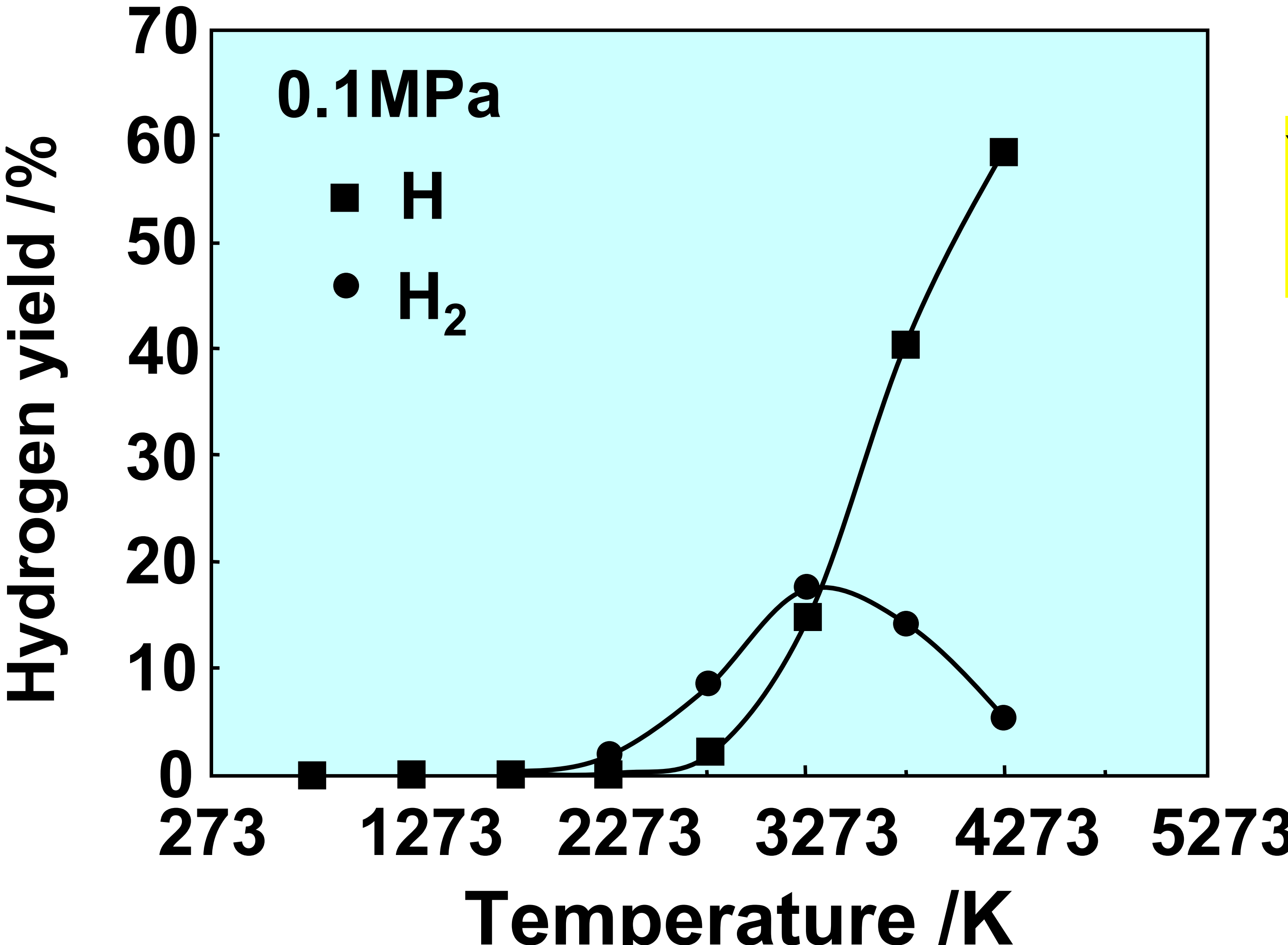


# 4.1 $NH_3$ production



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

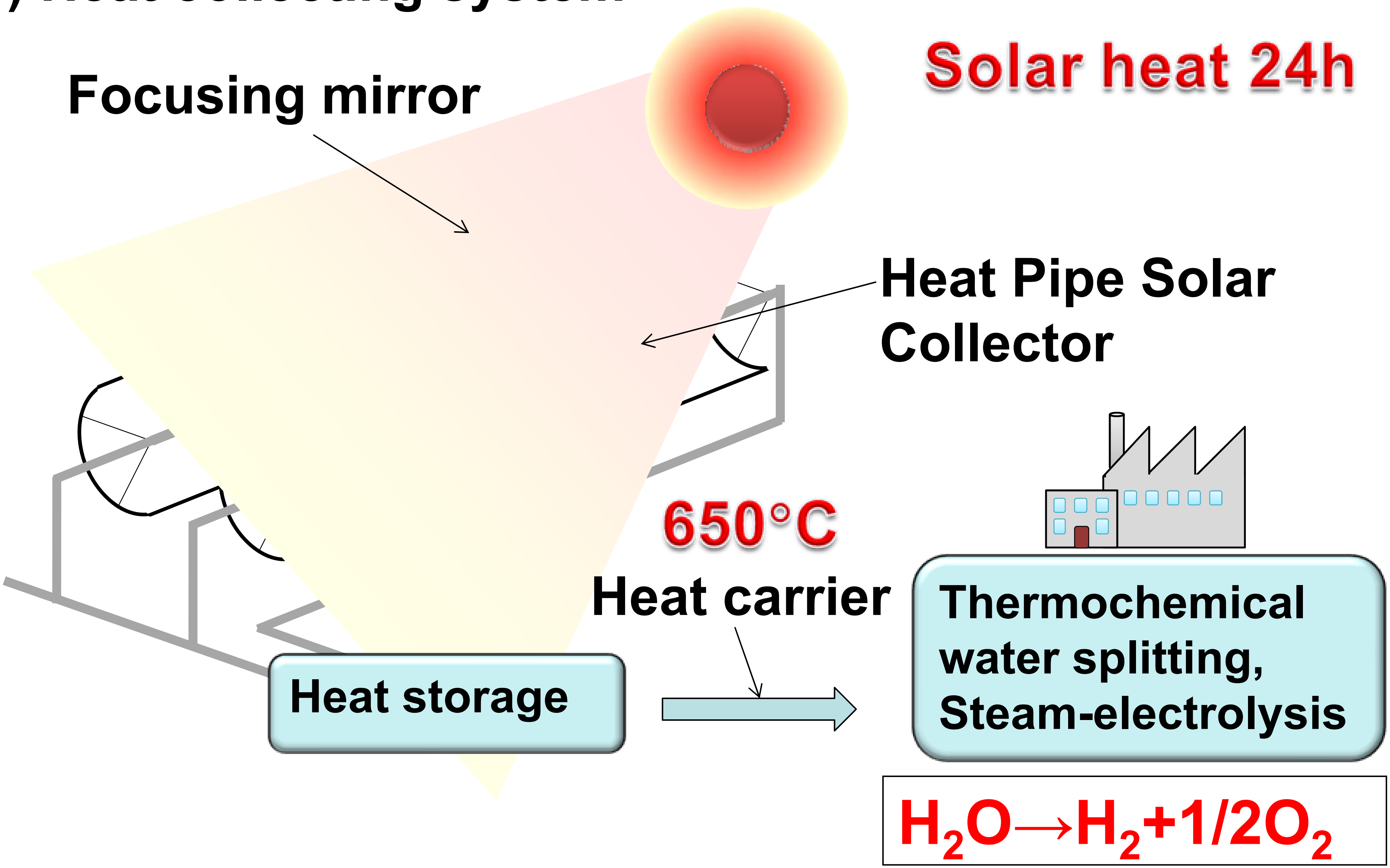



**Yield:64% at 4000°C**

↓

**Below 650°C**

# (1) Heat collecting system




**Iodine–Sulfur thermochemical water-splitting process**

# (2) Hydrogen and ammonia production

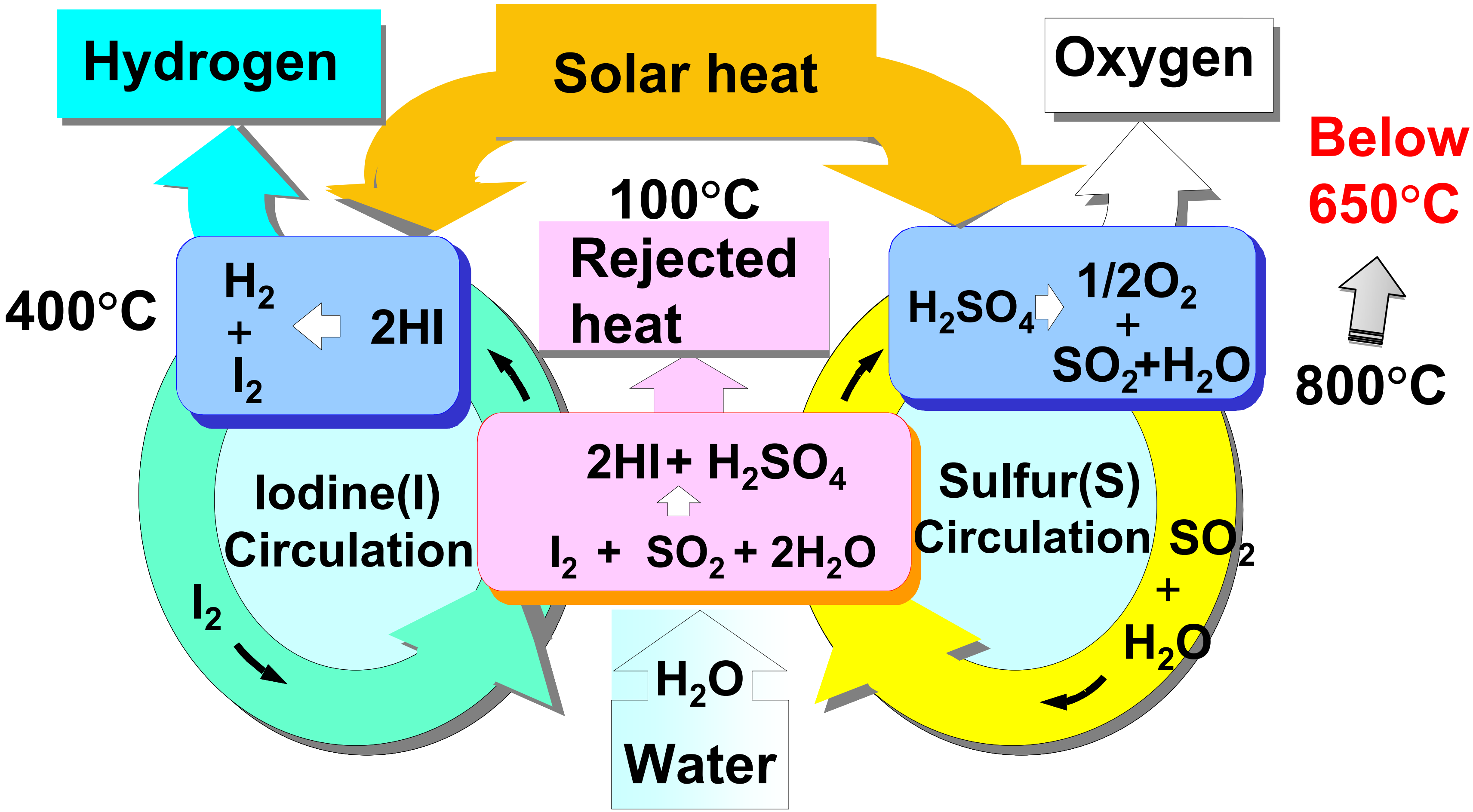
## Iodine–Sulfur thermochemical water-splitting process

Hydrogen iodide

$2HI \rightarrow I_2 + H_2$ (1)

Sulfuric acid $H_2SO_4 \rightarrow SO_3 + H_2O$

$\rightarrow SO_2 + 0.5O_2 + H_2O$ (2)




$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ (3)

## ■$H_2O$-Na oxide system

The possibility of $H_2$ production below 500 °C by water-splitting via reactions of the $H_2O$-Na oxides system was experimentally demonstrated.

□ $2NaOH + 2Na(l) \rightarrow 2Na_2O + H_2$

$H_2$ and $Na_2O$ were formed at 350 °C (20 h). : ~ 70 %

□ $2Na_2O \rightarrow Na_2O_2 + 2Na(g)$

Na can be generated at 500 °C (20 h). : ~ 70 %

□ $Na_2O_2 + H_2O(l) \rightarrow 2NaOH + 1/2O_2$

The hydrolysis can be completed at 100 °C. : ~ 100 %

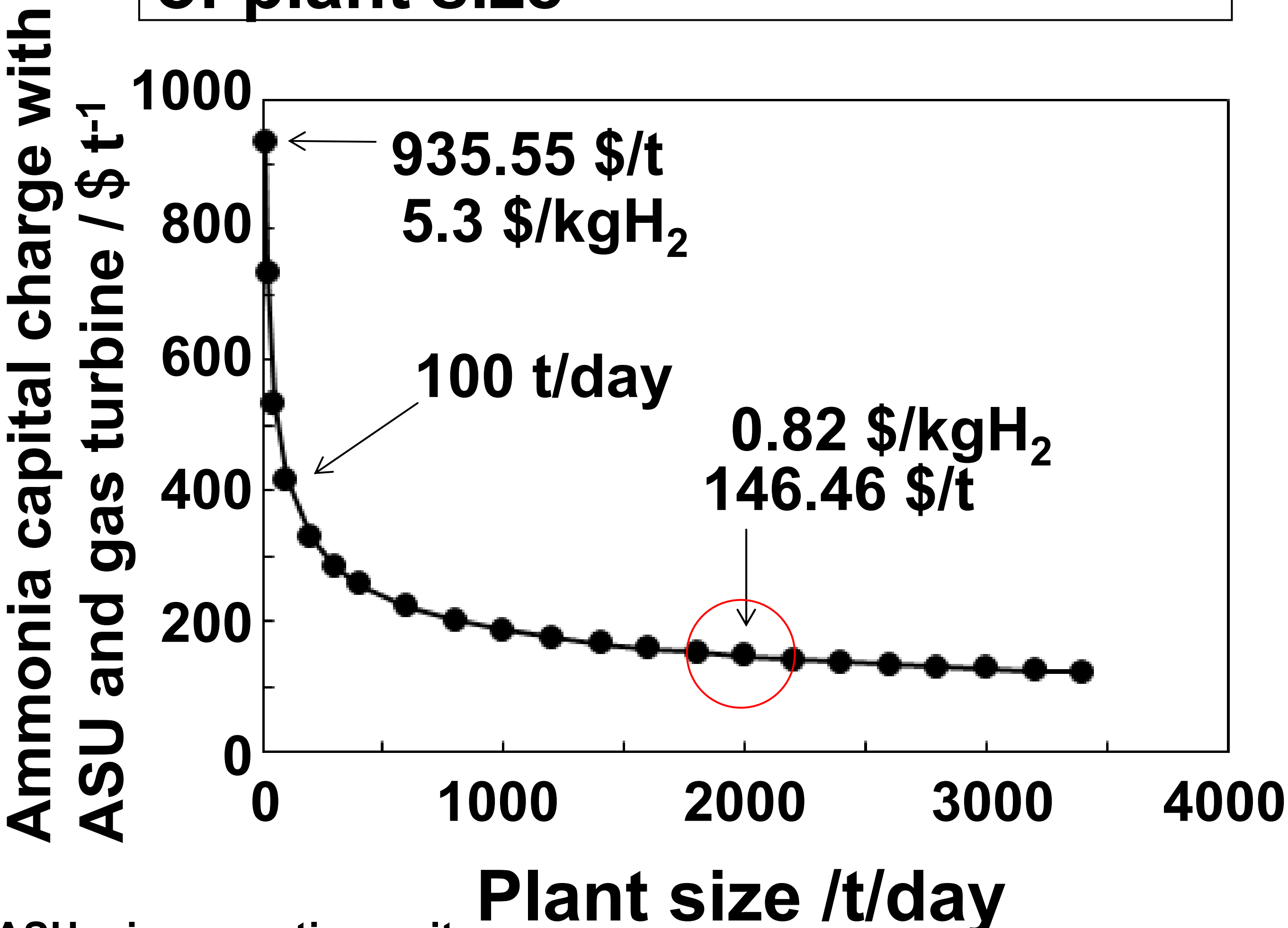
$$H_2O \rightarrow H_2 + 1/2O_2$$

Haber-Bosch process

H. Miyaoka, T. Ichikawa, N. Nakamura, Y. Kojima, "Low-Temperature water-splitting by sodium redox reaction", Int. J. Hydrogen Energy, 37, 17709-17714 (2012)

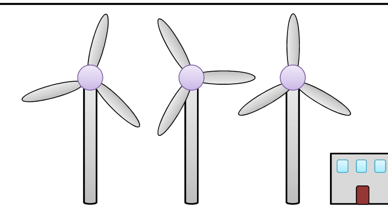
# Surplus electricity storage using $NH_3$ for high efficiency utilization

**Cost of ammonia as a function of plant size**




ASU: air separation unit

**A small-scale ammonia synthesis process**



**Cost of ammonia drastically increases below the plant size of 100t/day.**

# 4.2 $NH_3$ utilization

## (1) Hydrogen carrier for Fuel Cell Vehicles

### Specifications of hydrogen fuel for FCV

| Specifications | | ISO14687-2 |
|---|---|---|
| Hydrogen purity | | 99.97% |
| Non-hydrogen components | Hydro carbon(C1) | 2ppm |
| | Water ( $H_2O$) | 5ppm |
| | Oxygen ( $O_2$) | 5ppm |
| | $N_2$ ( Ar) | 100ppm |
| | He | 300ppm |
| | Carbon dioxide($CO_2$) | 2ppm |
| | Carbon monooxide(CO) | 0.2ppm |
| | Sulfur compound | 0.004ppm |
| | Formaldehyde | 0.01ppm |
| | Formic acid | 0.2ppm |
| | Ammonia | 0.1ppm |
| | Halide | 0.05ppm |

International Standard, December 2012

Ammonia concentration: <0.1ppm

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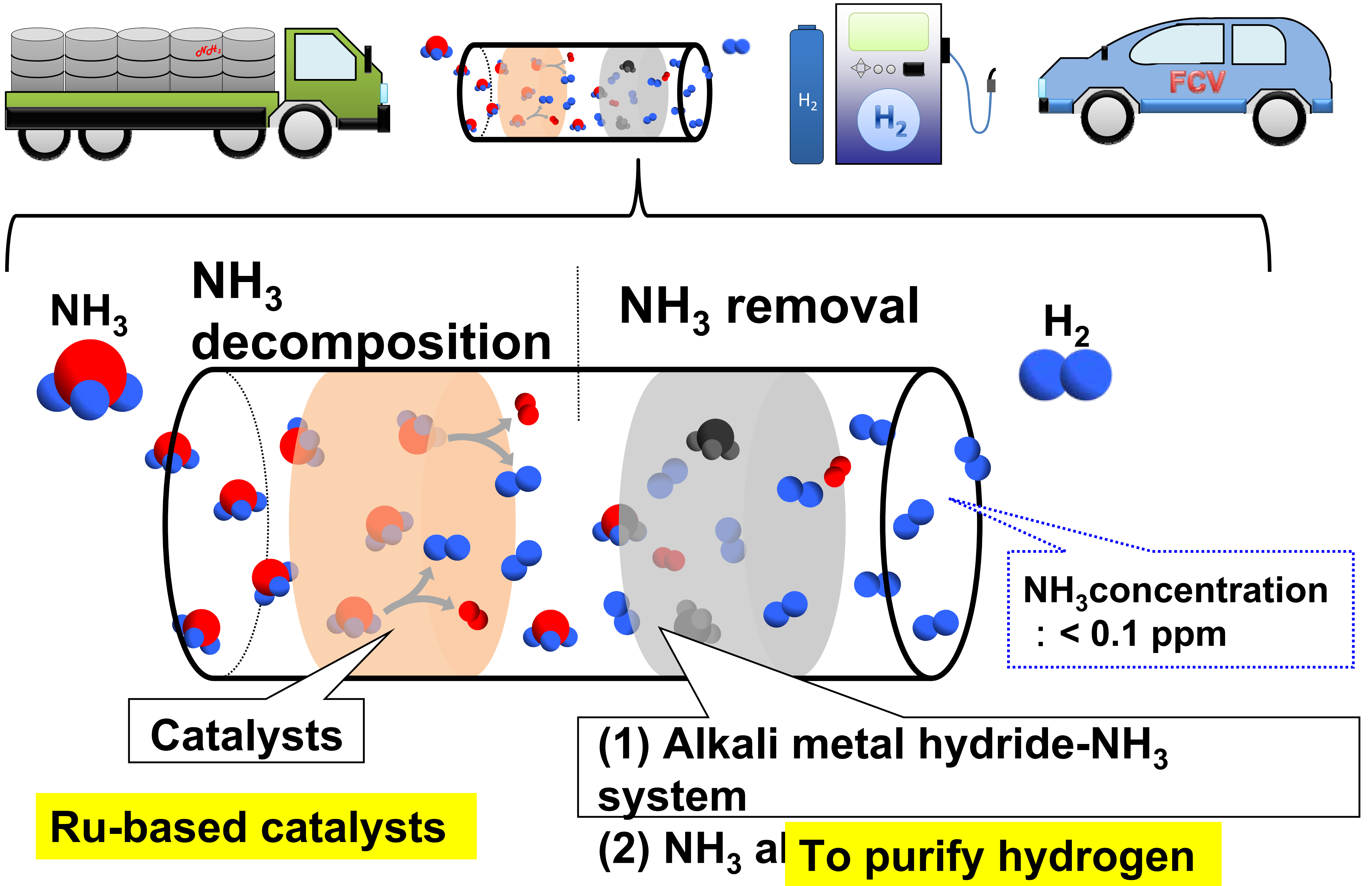

(1) $LiH-NH_3$ system

**523-573K, 0.5MPa, $H_2$ flow**

$LiH + NH_3 \rightarrow LiNH_2 + H_2$ (1)

**$H_2$ generation at room temperature**

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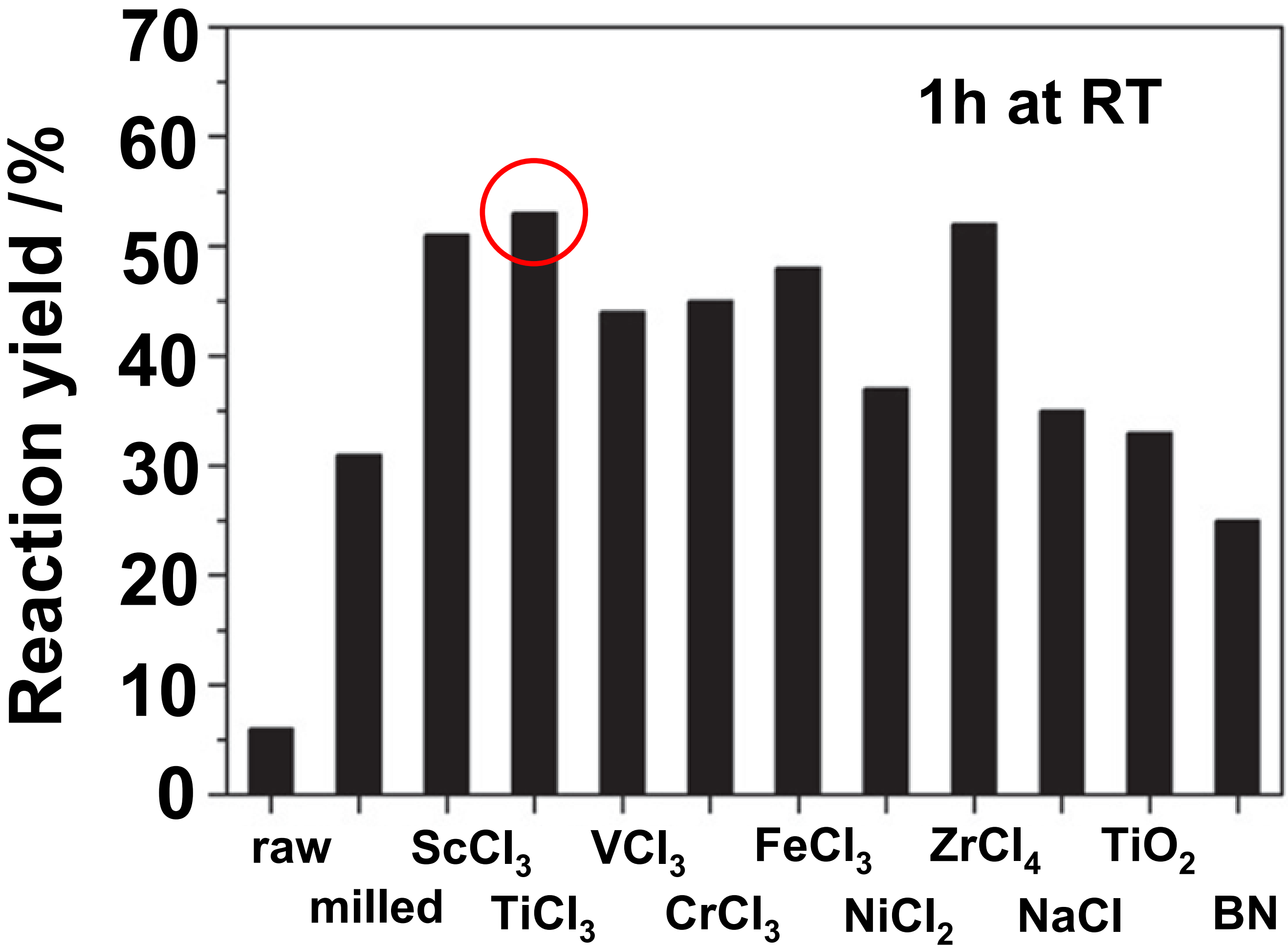
**Reaction yield of $LiH-NH_3$ system using additives**




$\Delta H^0$: $-43 kJ/molH_2$
$H_2$ content: 8.1mass%


Y. Kojima, K. Tange, S. Hino, S. Isobe, M. Tsubota, K. Nakamura, M. Nakatake, H. Miyaoka, H. Yamamoto and T. Ichikawa, J. Mater. Res., 24, 2185 (2009)
H. Miyaoka, H. Fujii, H. Yamamoto, S. Hino, H. Nakanishi, T. Ichikawa, Y. Kojima, Int. J. Hydrogen Energy 37, 16025-16030 (2012)

# (2) $NH_3$ absorbing materials

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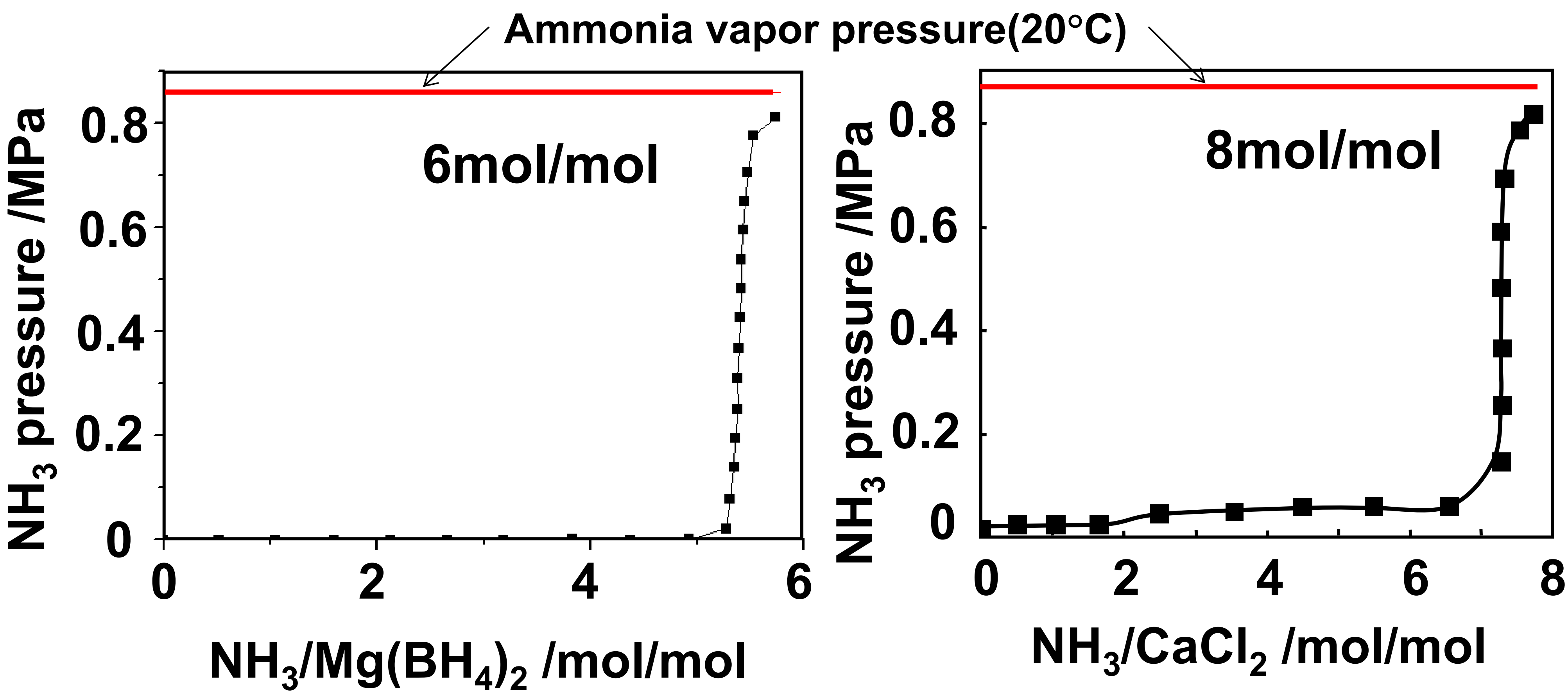
## P-C isotherms for $Mg(BH_4)_2$-$NH_3$ and $CaCl_2$-$NH_3$ systems




**$NH_3$ storage capacity: 65wt% 55wt%**

T. Aoki et ai., Abstract of MH2012, Kyoto Japan (2012)

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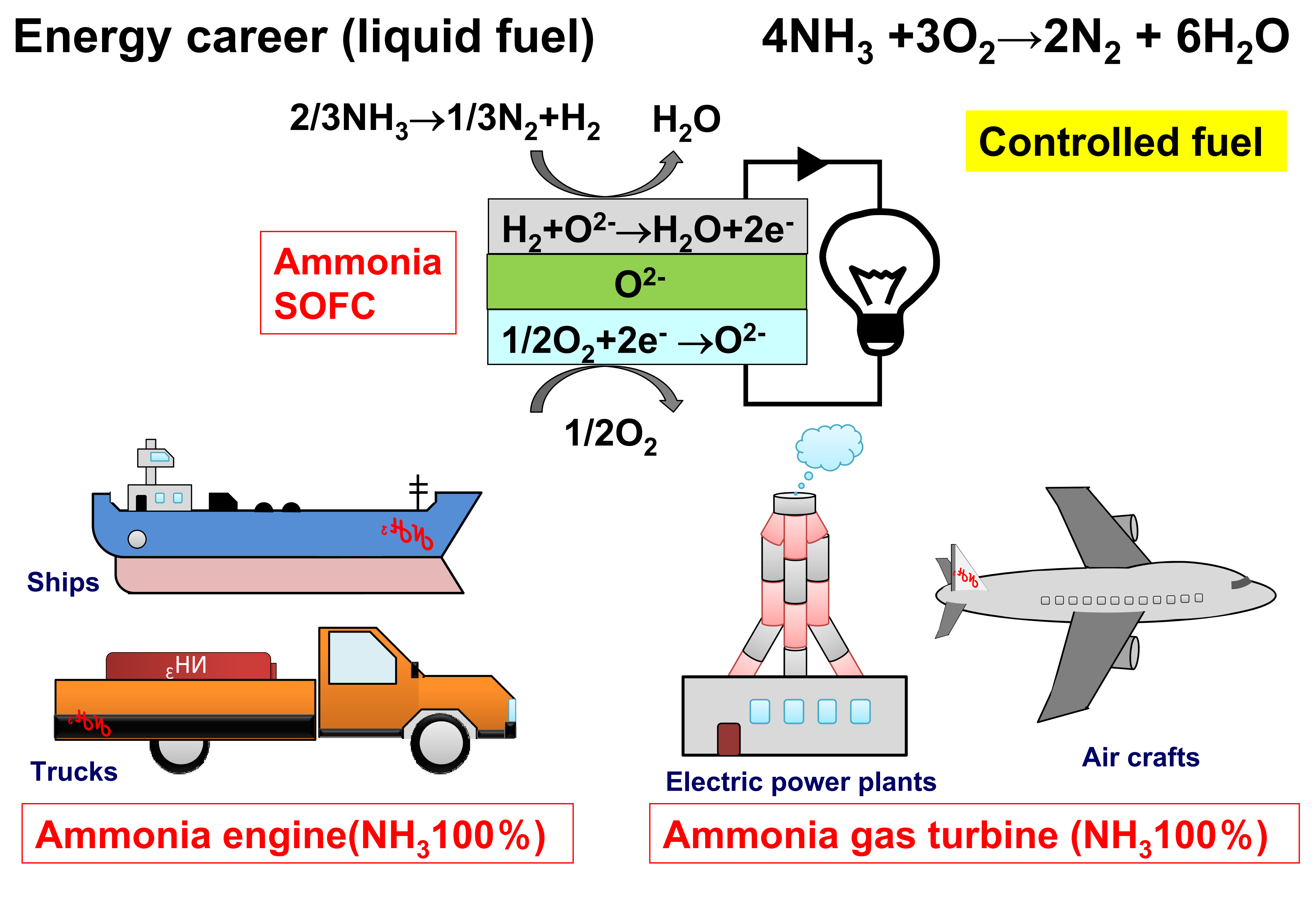
# Ammonia absorption behavior in $CaCl_2$

7mm



Energy career (liquid fuel)
$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
$2/3NH_3 \rightarrow 1/3N_2 + H_2$
$H_2O$
Controlled fuel
Ammonia SOFC
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
$O^{2-}$
$1/2O_2 + 2e^- \rightarrow O^{2-}$
$1/2O_2$
Ships
Trucks
Electric power plants
Air crafts
Ammonia engine($NH_3$100%)
Ammonia gas turbine ($NH_3$100%)

# 5.Summary

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1. Ammonia has been expected as an energy carrier because it has a high $H_2$ storage capacity with 17.8 mass% and the volumetric hydrogen density is 1.5-2.2 times of liquid hydrogen.
2. $CO_2$ free hydrogen (ammonia) will be synthesized using solar heat below 650°C.
3. A small-scale ammonia synthesis process will be developed to store various renewable energies.
4. Ammonia has advantages in cost and convenience as a renewable fuel for fuel cell vehicles, SOFC, electric power plants, air crafts, ships and trucks.

Power to liquid $NH_3$ is a promising technology which converts electrical power to fuel.

# Website

## Emerging Alternative Fuels

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Several emerging alternative fuels are under development or already developed and may be available in the United States. These fuels may increase energy security, reduce emissions, improve vehicle performance, and stimulate the U.S. economy.

Some of these emerging fuels are alternative fuels under the Energy Policy Act of 1992 and may qualify for federal and state incentives and laws:

- Biobutanol
- Drop-In Biofuels
- Methanol
- P-Series Fuels
- Renewable Natural Gas (Biogas)
- xTL Fuels (Fischer-Tropsch)

**The use of ammonia as a potential hydrogen carrier for hydrogen delivery or off-board hydrogen storage was evaluated by the DOE.**
**$NH_3$: Emerging Alternative Fuel**

Additional fuels used in limited quantities may meet the criteria for alternative fuels, including but not limited to ammonia, diethylene glycol dimethyl ether (diglyme), and dimethyl ether (DME). More research is needed to characterize the impacts of these fuels, such as necessary vehicle modifications, required fueling infrastructure, human health impacts, greenhouse gas emissions, and tailpipe emissions.

JST Japan Science and Technology Agency

ALCA Advanced Low Carbon Technology Research and Development Program

## Energy Carrier

**Year Started: 2013**

# Thank you for your attention.

http://www.afdc.energy.gov/afdc/fuels/emerging.html