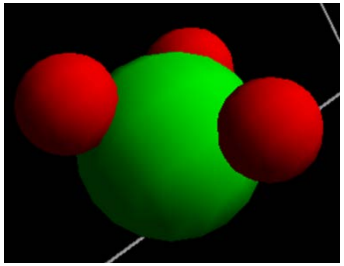
Liquid Ammonia for Hydrogen Storage



21-24 of September 2014

11th Annual NH_3 Fuel Association Conference

Yoshitsugu Kojima

Hiroshima University

Institute for Advanced Materials Research

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Hiroshima Peace Memorial

Itsukushima Shinto Shrine

Peace Memorial City

1. Energy and Environmental Issues

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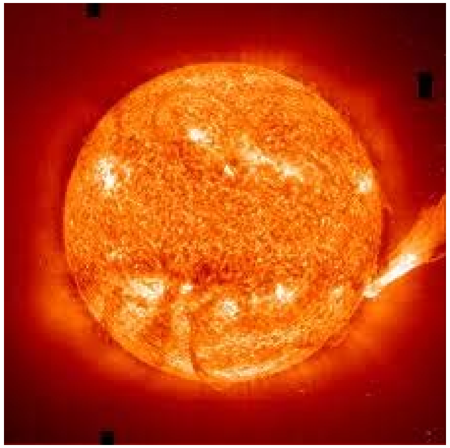
Energy and Environmental Issues Renewable energy



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

Wind

Geothermal

Hydro

Solar thermal

Solar cell

Tidal power

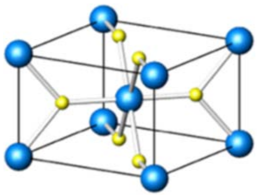
Wave power

Electric power

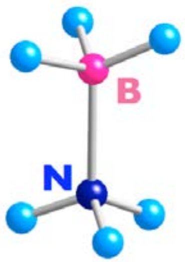
Hydrogen (gas)→ Hydrogen carrier (solid, liquid)

2. Research on hydrogen carrier (hydrogen storage materials) and systems (1999～2014)

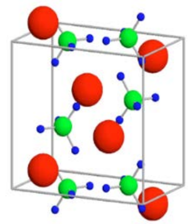
Inorganic hydrides (thermolysis)



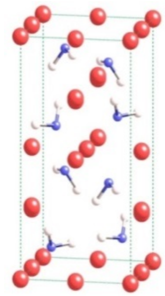
MgH_2



NH_3BH_3

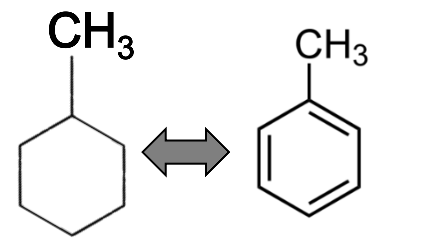


$LiBH_4$

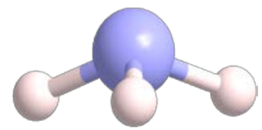


$LiNH_2$

Organic hydrides

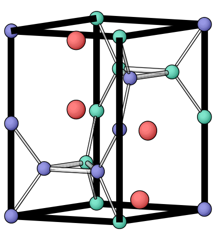


Methylcyclohexane⇔ Toluene

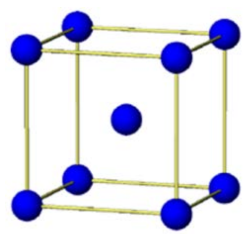


NH_3

Hydrogen absorbing alloys

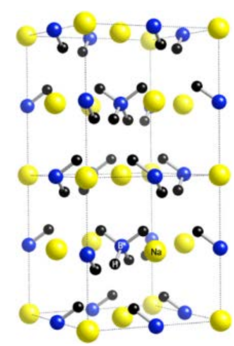


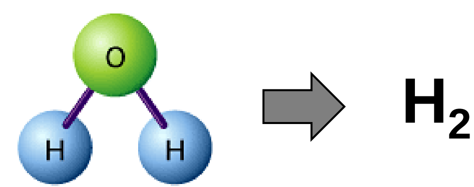
Ti-Cr-Mn(AB_2)



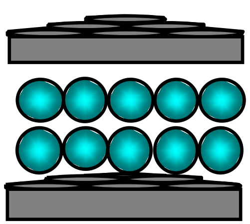
Ti-Cr-V(BCC)

Inorganic hydrides (hydrolysis)

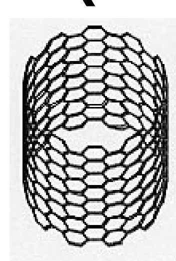




Carbon materials (77K)



Carbon



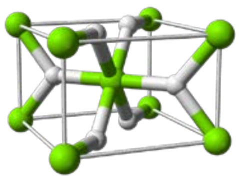
200 kinds of hydrogen storage materials

Y. Kojima, H. Miyaoka, T. Ichikawa: "Hydrogen Storage Materials". In Steven L. Suib editor. New and Future Developments in Catalysis: Batteries, Hydrogen Storage and Fuel Cells Amsterdam, Elsevier, 2013.

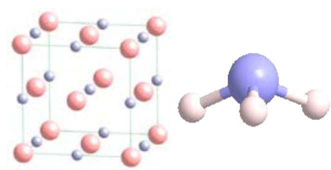
Thermolysis of inorganic hydrides

Control heat of formation and kinetics

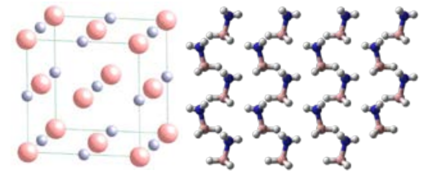
Mg-based nano-comoposite Material(Nb_2O_5:1mol%)



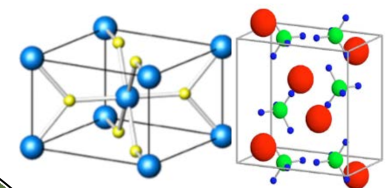
$LiH-NH_3$

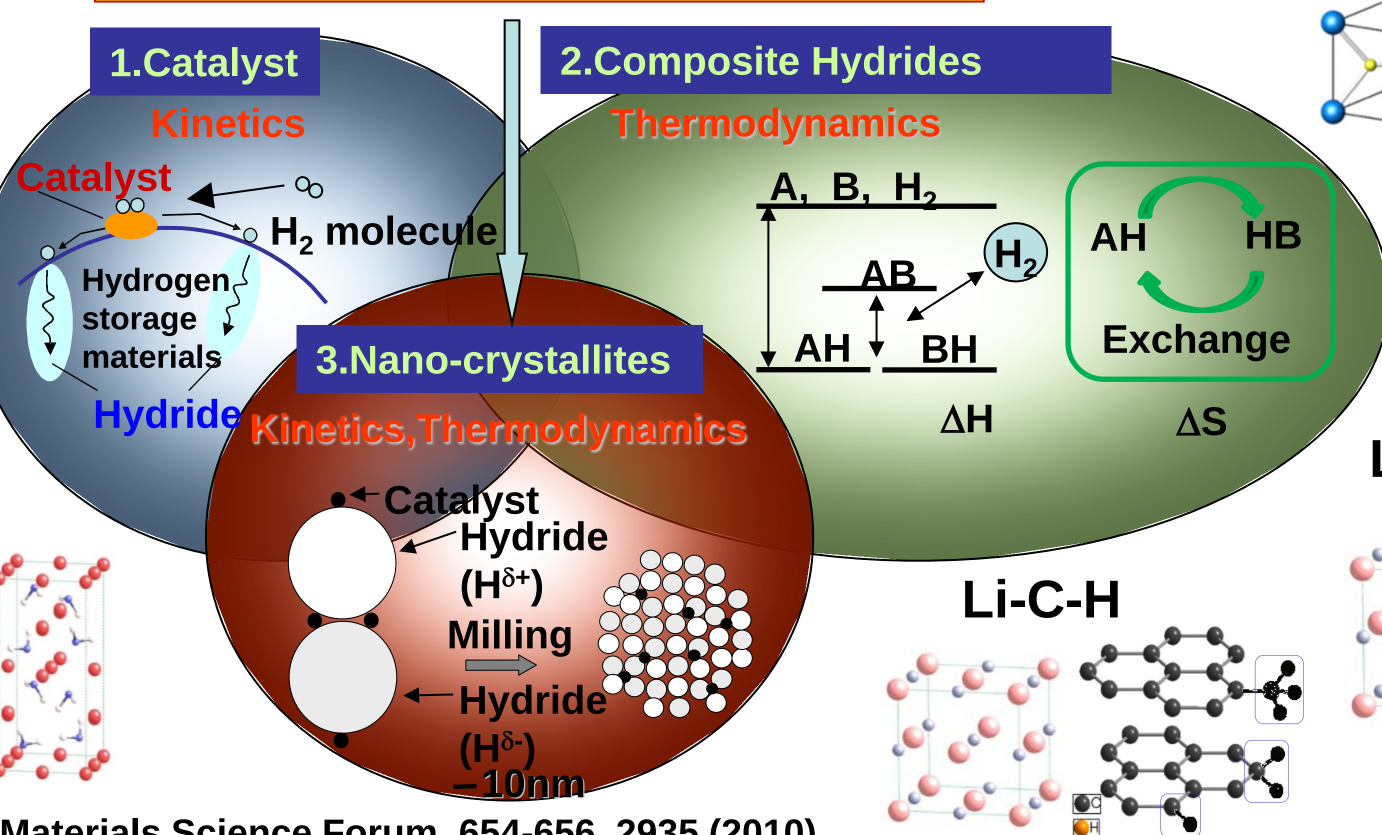


$NaH-NH_3BH_3$

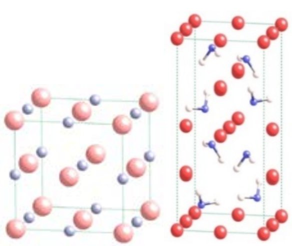


$2LiBH_4-MgH_2$

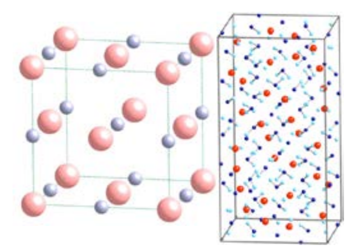




Li-N-H

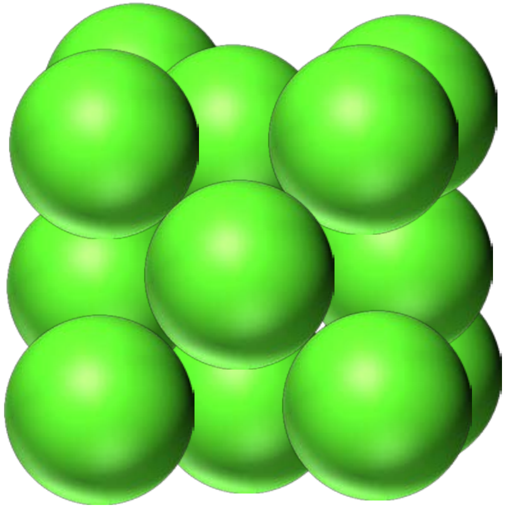


Li-Mg-N-H



Y. Kojima, Materials Science Forum, 654-656, 2935 (2010)

Packing ratio

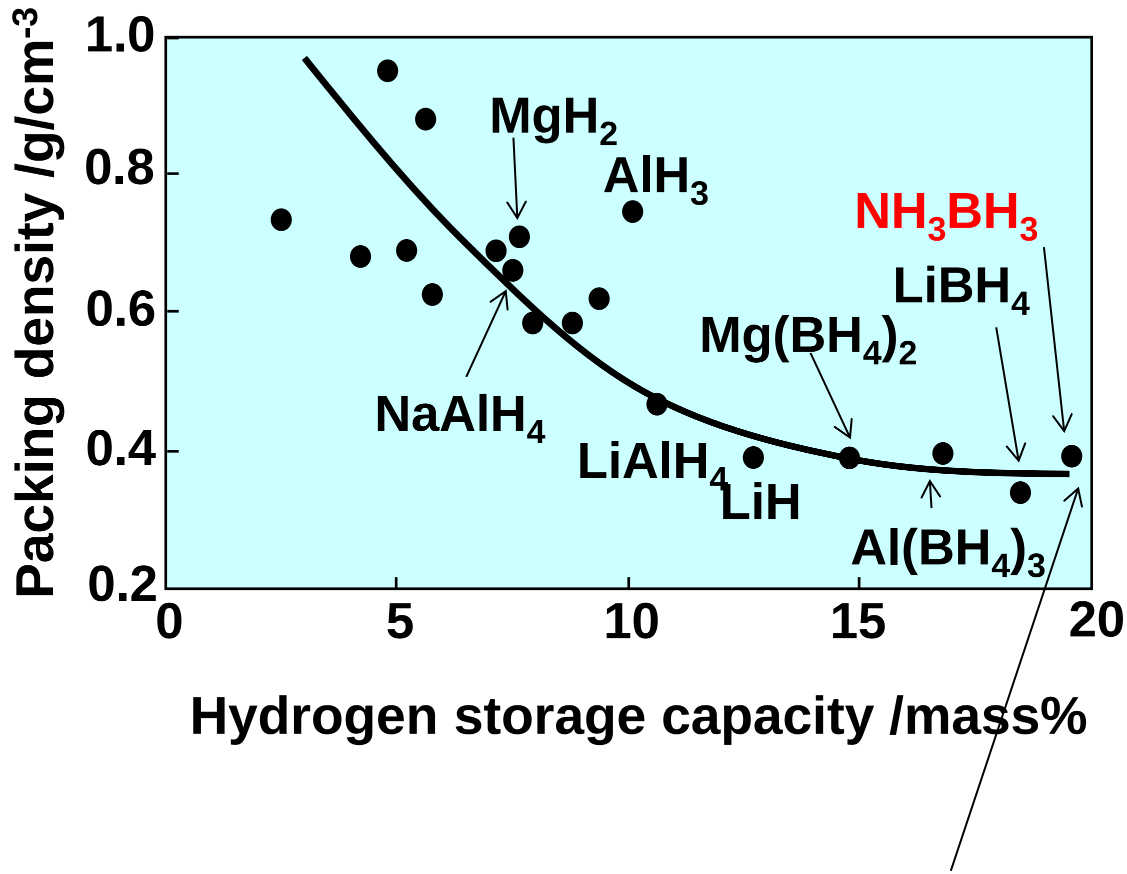


Face-centered cubic structure

Packing ratio: 74% (theoretical value)

Packing ratio: 50% (practical value)

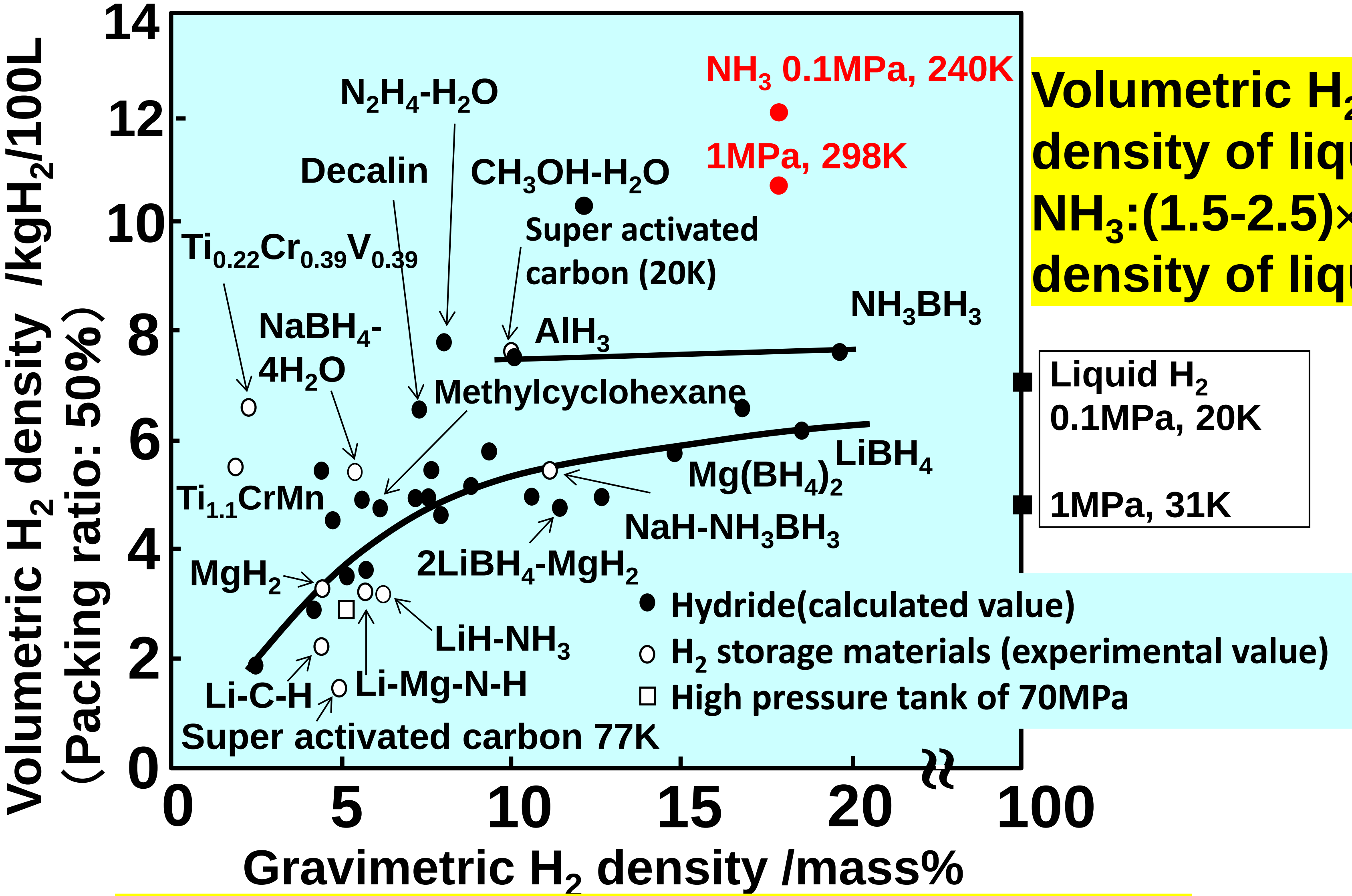
Packing densities of solid-state hydrides with light elements



Volumetric H_2 density : below $8kgH_2/100L$

3. Properties and Safety of Ammonia

H_2 densities of hydrogen carrier(solid, liquid)



Volumetric H_2 density of liquid NH_3:(1.5-2.5)×H_2 density of liquid H_2

NH_3: burnable substance → Energy carrier

Ammonia tank

10mass%, 8.2kgH_2/100L

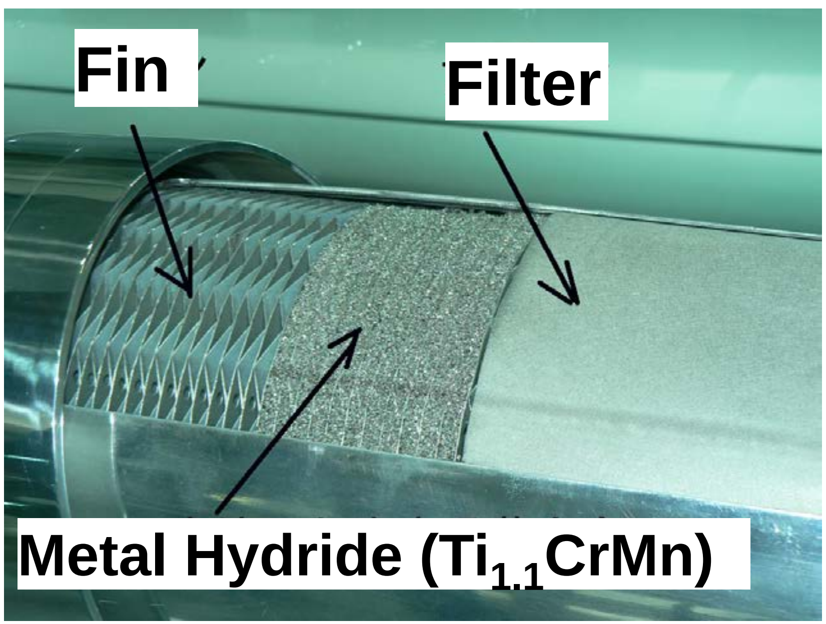
V

High pressure H_2 tank(70MPa)

5mass%, 2.8kgH_2/100L

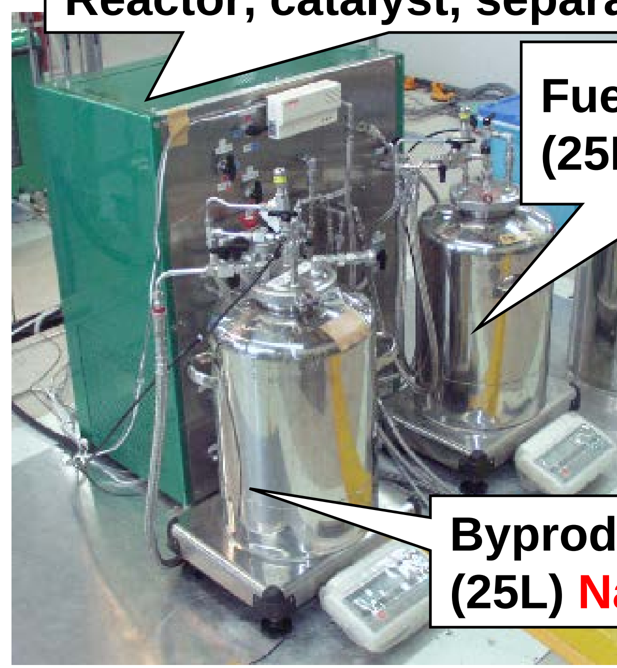
V

High-pressure MH tank (Ti-Cr-Mn + compressed H_2)



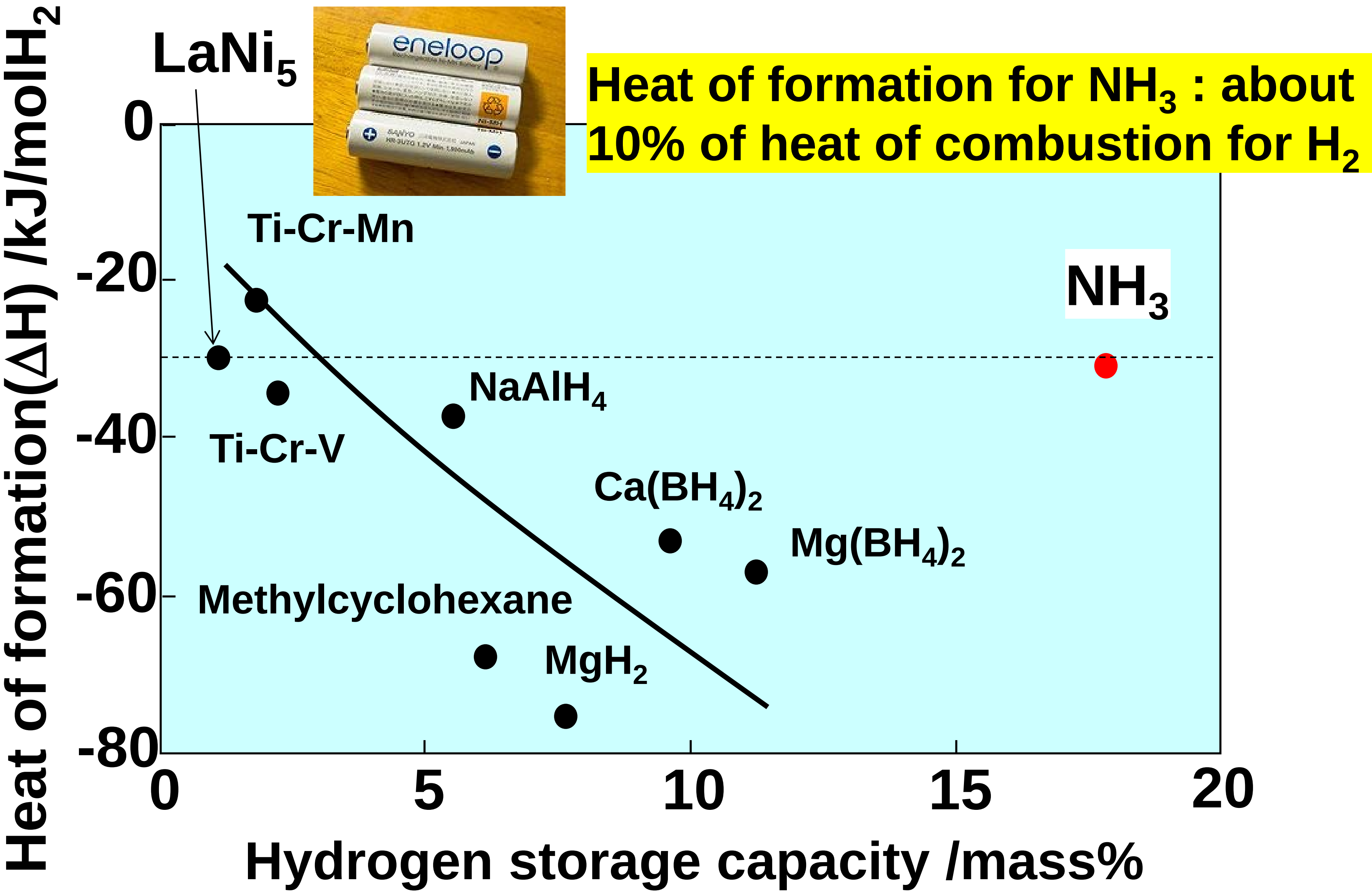
1.7mass%, 4.1kgH_2/100L

Hydrogen generator using sodium borohydride



2.0mass%, 1.5kgH_2/100L

Heat of formation and H_2 storage capacity



Costs of NH_3 and H_2

Item		NH_3	Hydrogen
Price in Japan(Yen/Nm^3H_2)		27-36(2013)	122
Production cost($/kg$H_2$) 2200ton/day USA		3.80	3.00
Transportation cost($/kg$H_2$)	1610km Pipe line USA	0.19	0.51-3.22 (1.87)
Storage cost ($/kg$H_2$) $H_2$2664ton	15 day USA	0.06	1.97
	182 day USA	0.54	14.95
Supply cost($/kg$H_2$) USA		4.05-4.53 <	5.5-21

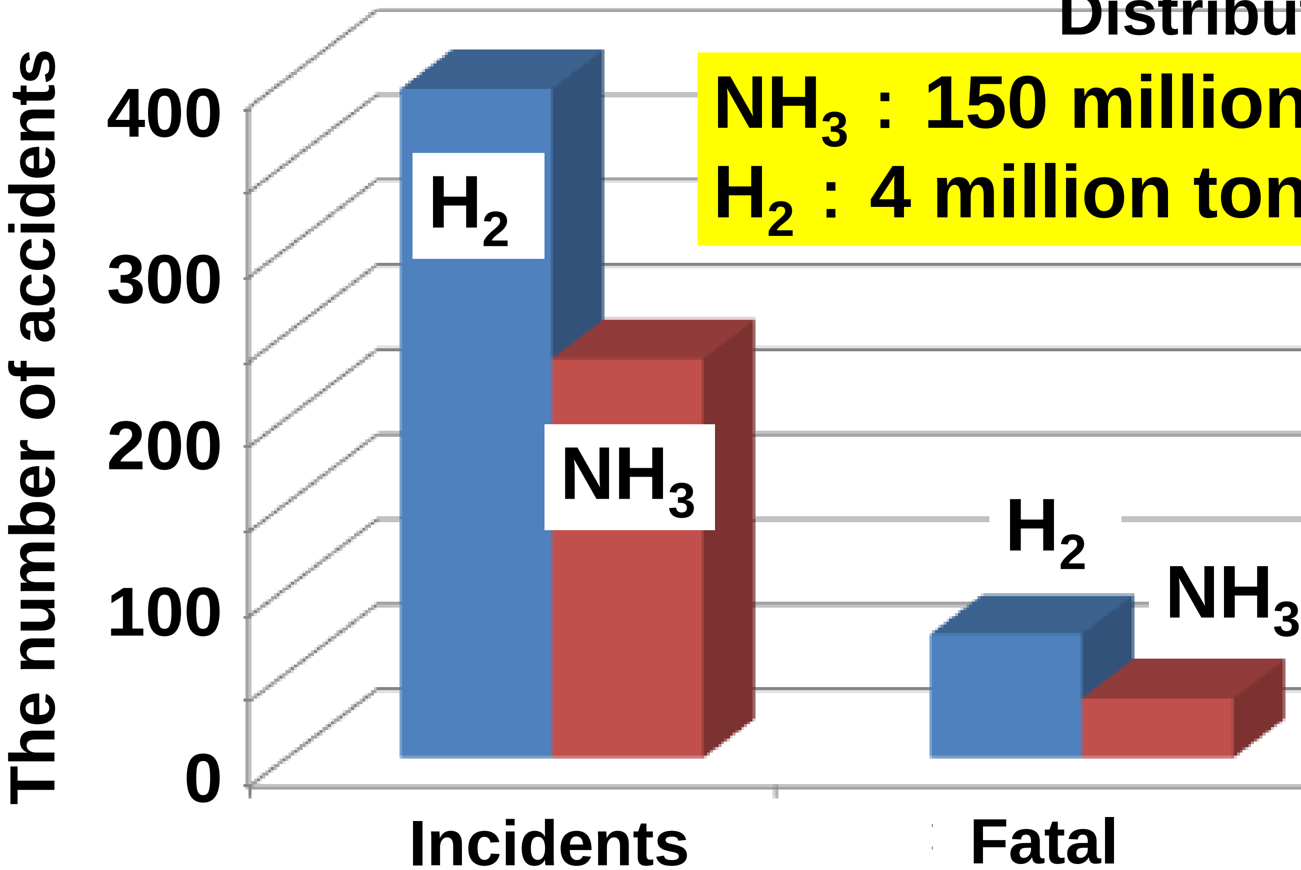
Cost of NH_3 in Japan: 20-30% of cost of H_2

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-)

Distribution amount

NH_3 : 150 million tonnes / year
H_2 : 4 million tonnes / year



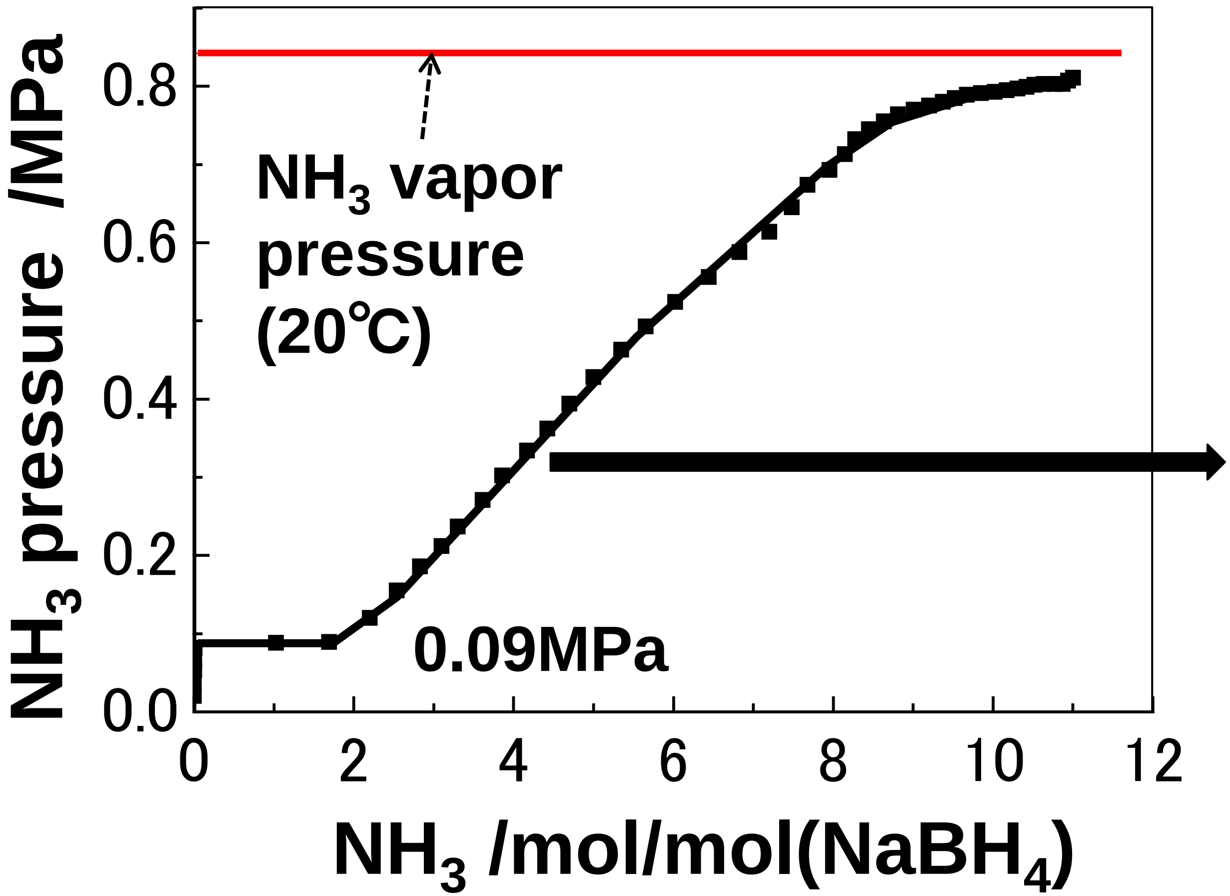
Controlled fuel

↑

Hazardous substance

http://www.elucidare.co.uk/news/Ammonia%20as%20H2%20carrier.pdf

P-C isotherm for $NaBH_4$-NH_3 system(ammine complex)



$NaBH_4$ solution

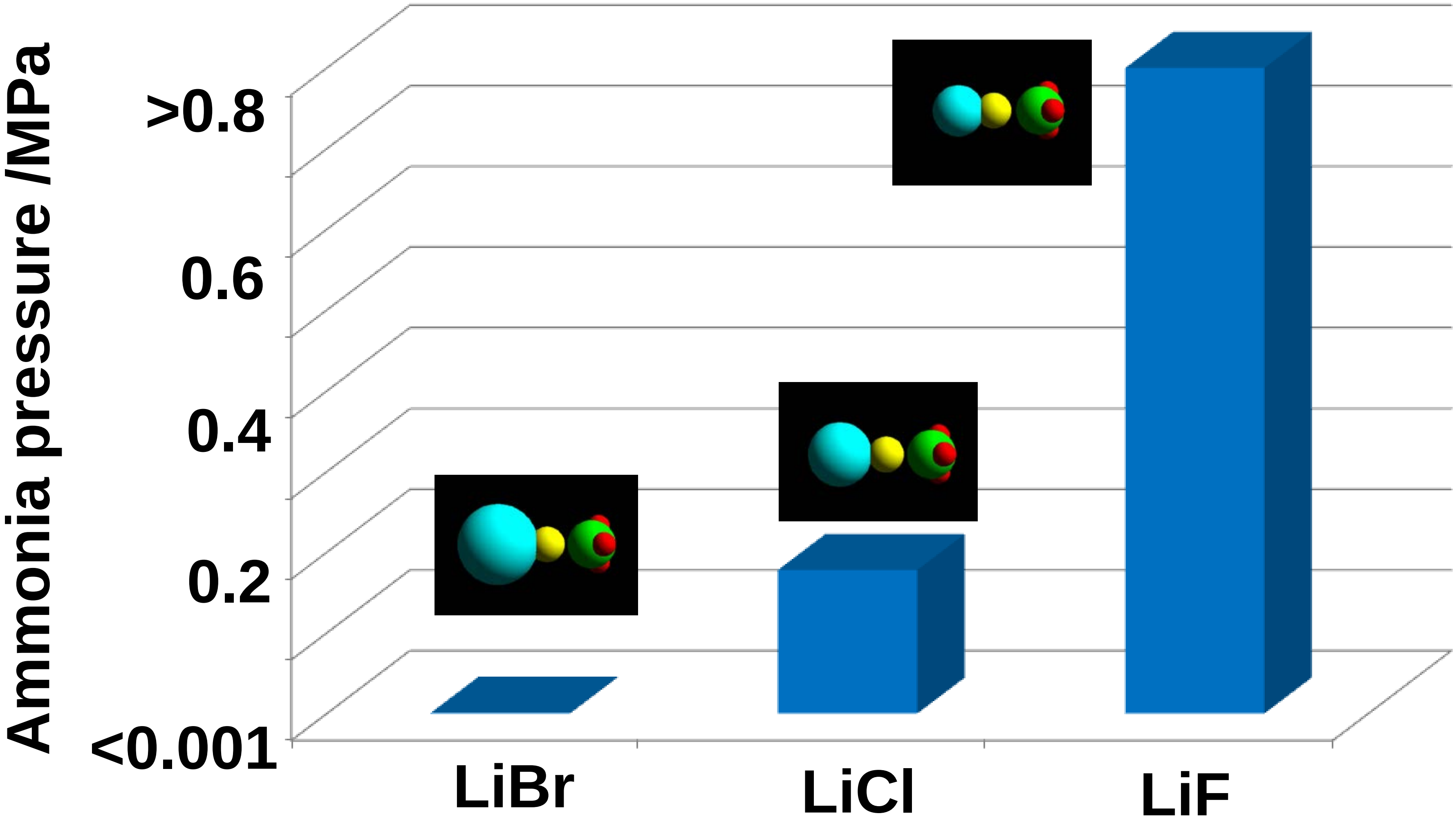
Atmospheric pressure

NH_3 vapor pressure of $NaBH_4$ < NH_3 vapor pressure

Safer ammonia

T. Aoki, T. Ichikawa, H. Miyaoka, Y. Kojima, J. Phys. Chem. C 118, 18412-1846 (2014)

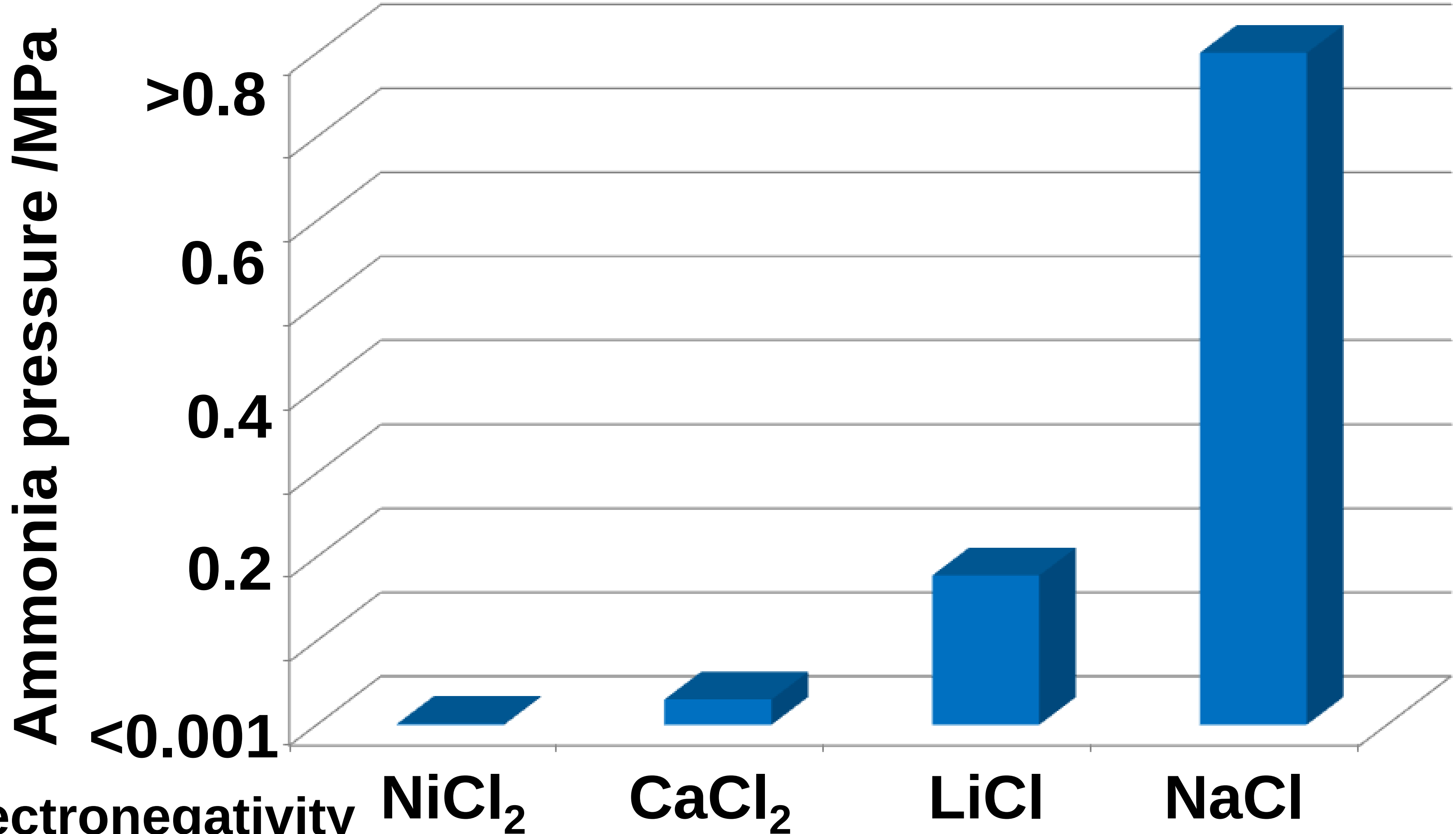
Plateau pressure of lithium ammine halide



Electronegativity difference(χ_p) 1.98 < 2.18 < 3

T. Aoki, T. Ichikawa, H. Miyaoka, Y. Kojima, J. Phys. Chem. C 118, 18412-1846 (2014)

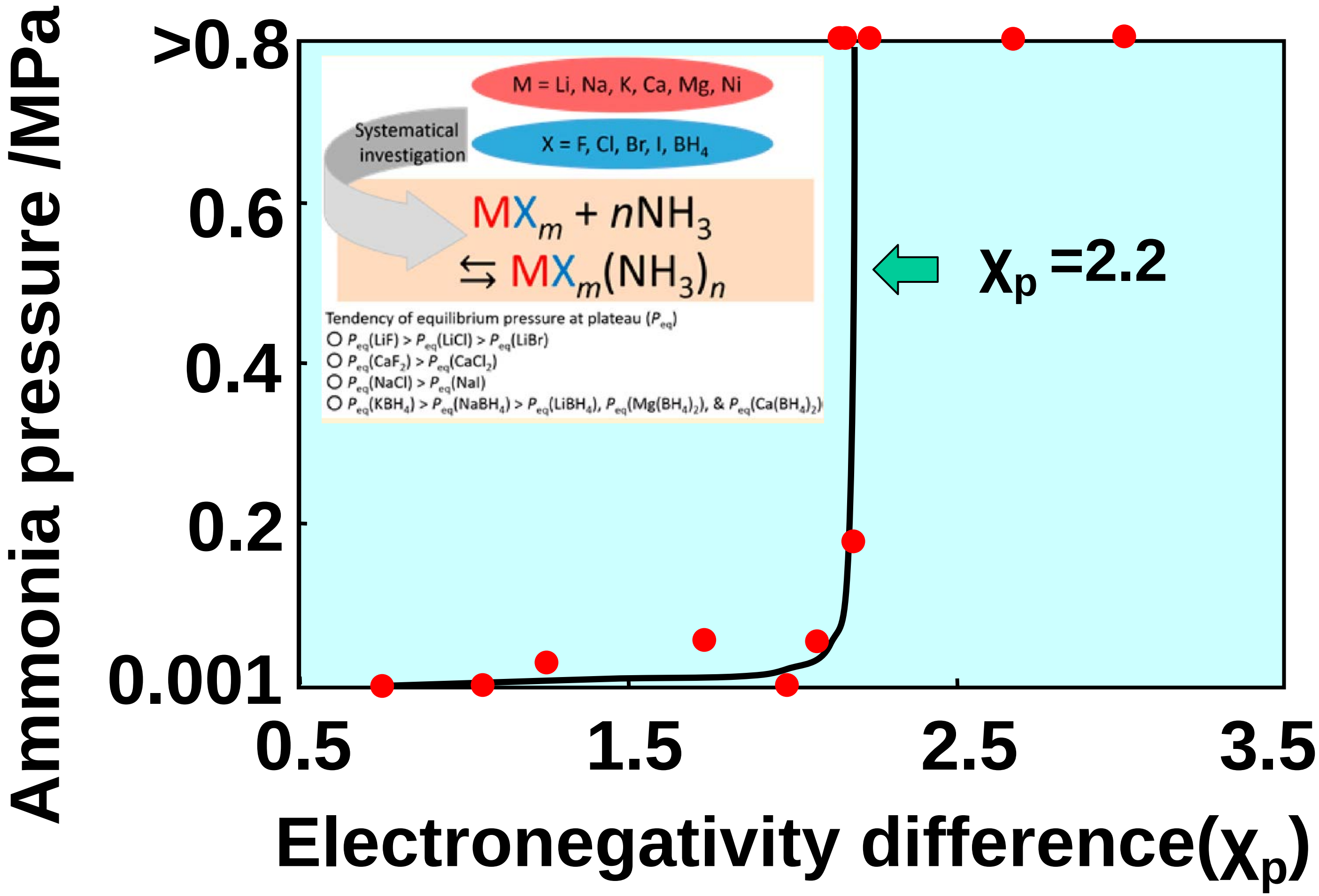
Plateau pressure of metal ammine chloride



Electronegativity difference(χ_p) **1.05 < 1.25 < 2.18 < 2.23**

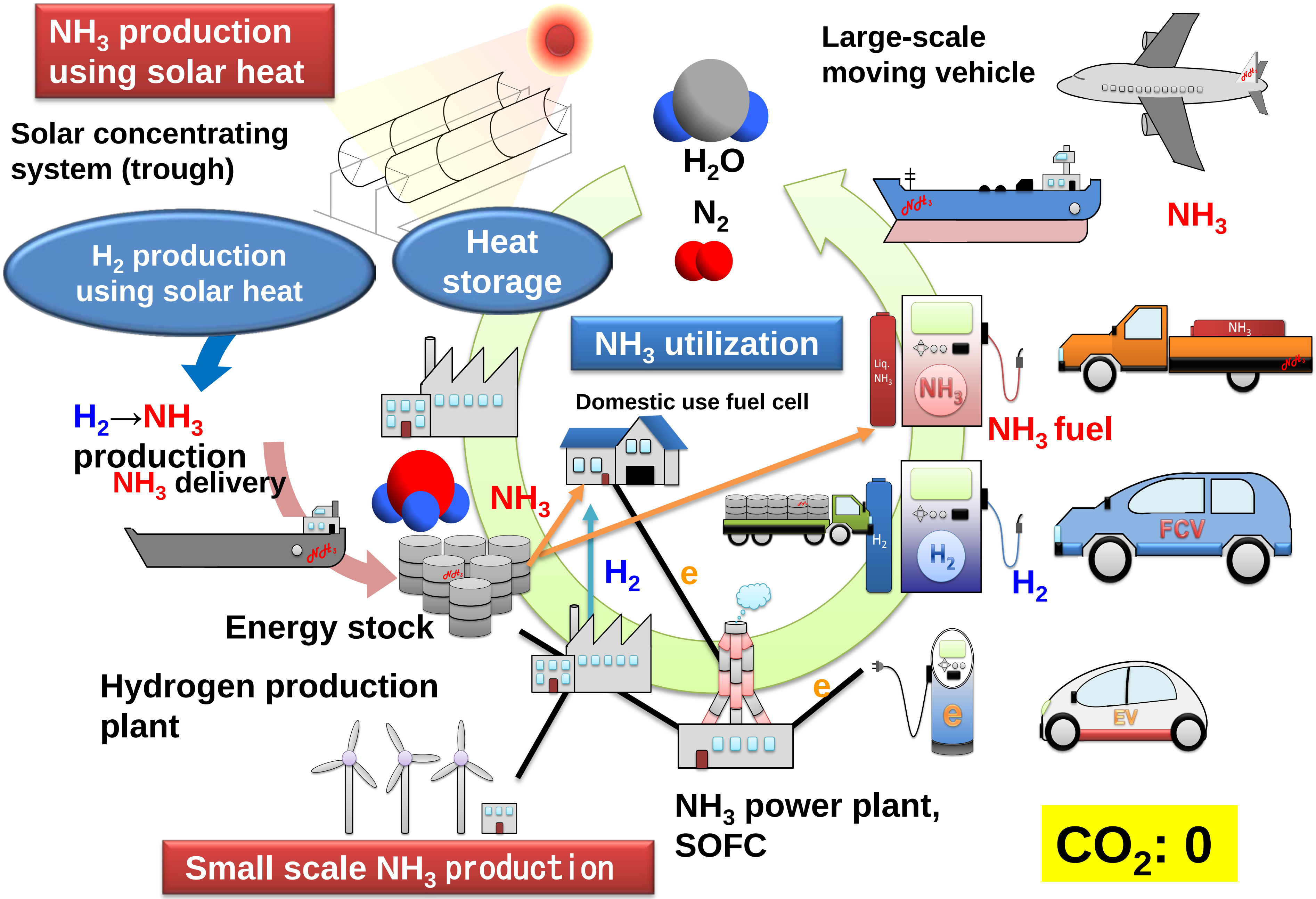
The smaller the electronegativity difference is, the lower plateau pressure is achieved. Safety improvement

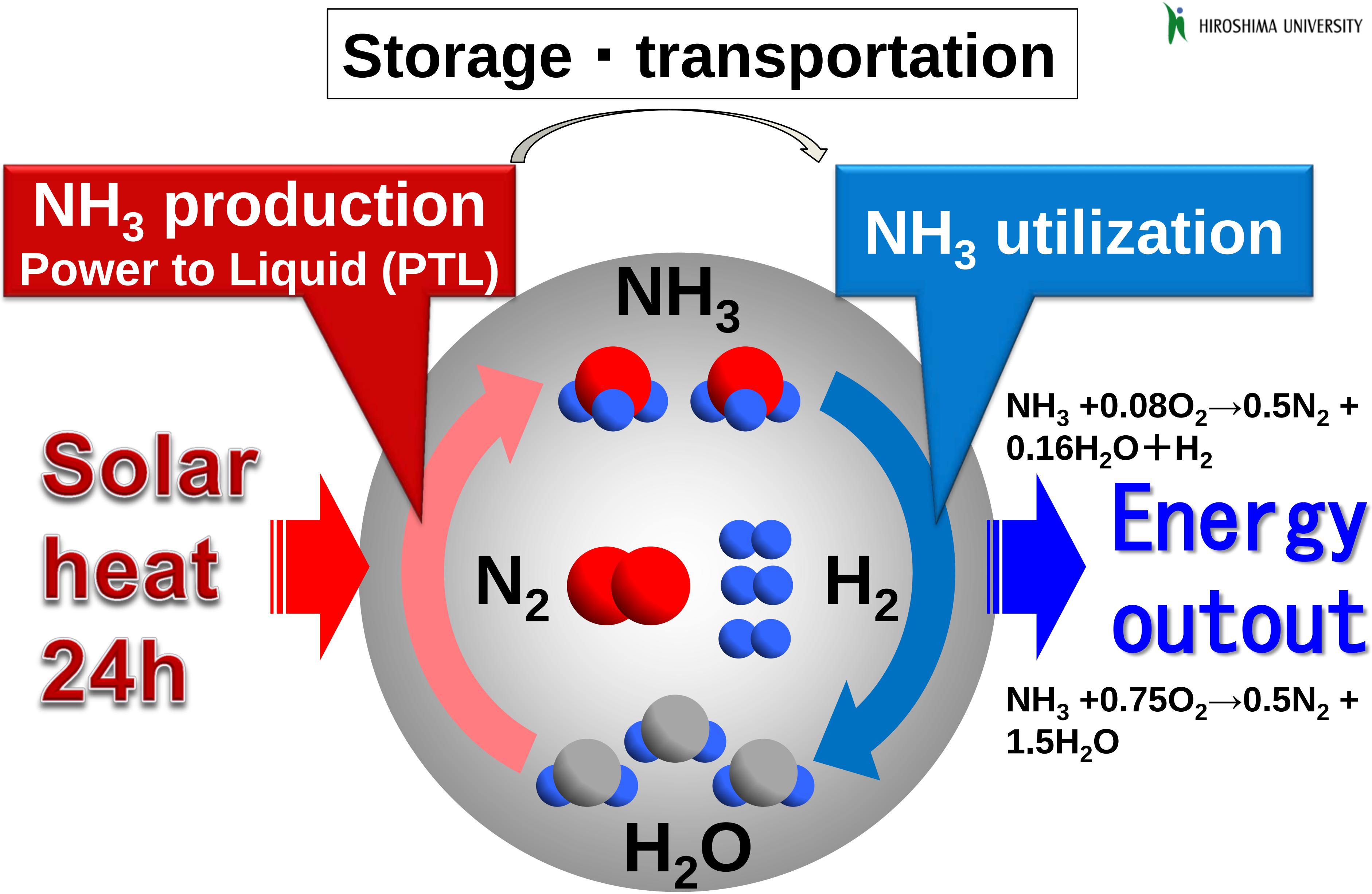
Plateau pressure vs electronegativity difference



Ammonia absorption: χ_p <2.2

4. Hydrogen Economy Using Ammonia

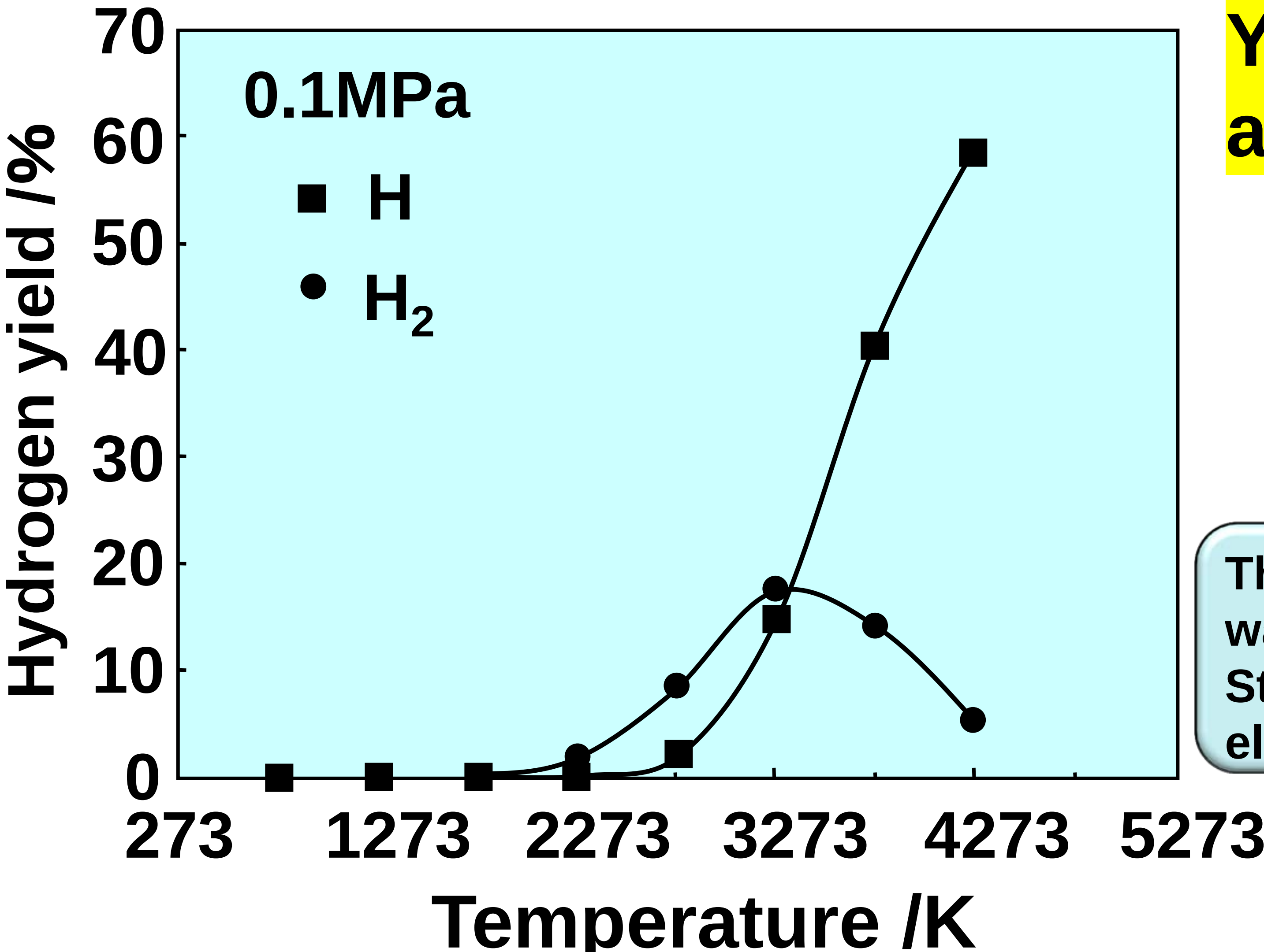




Conceptive picture of ammonia energy system

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

Thermochemical water splitting, Steam-electrolysis

M-Redox system

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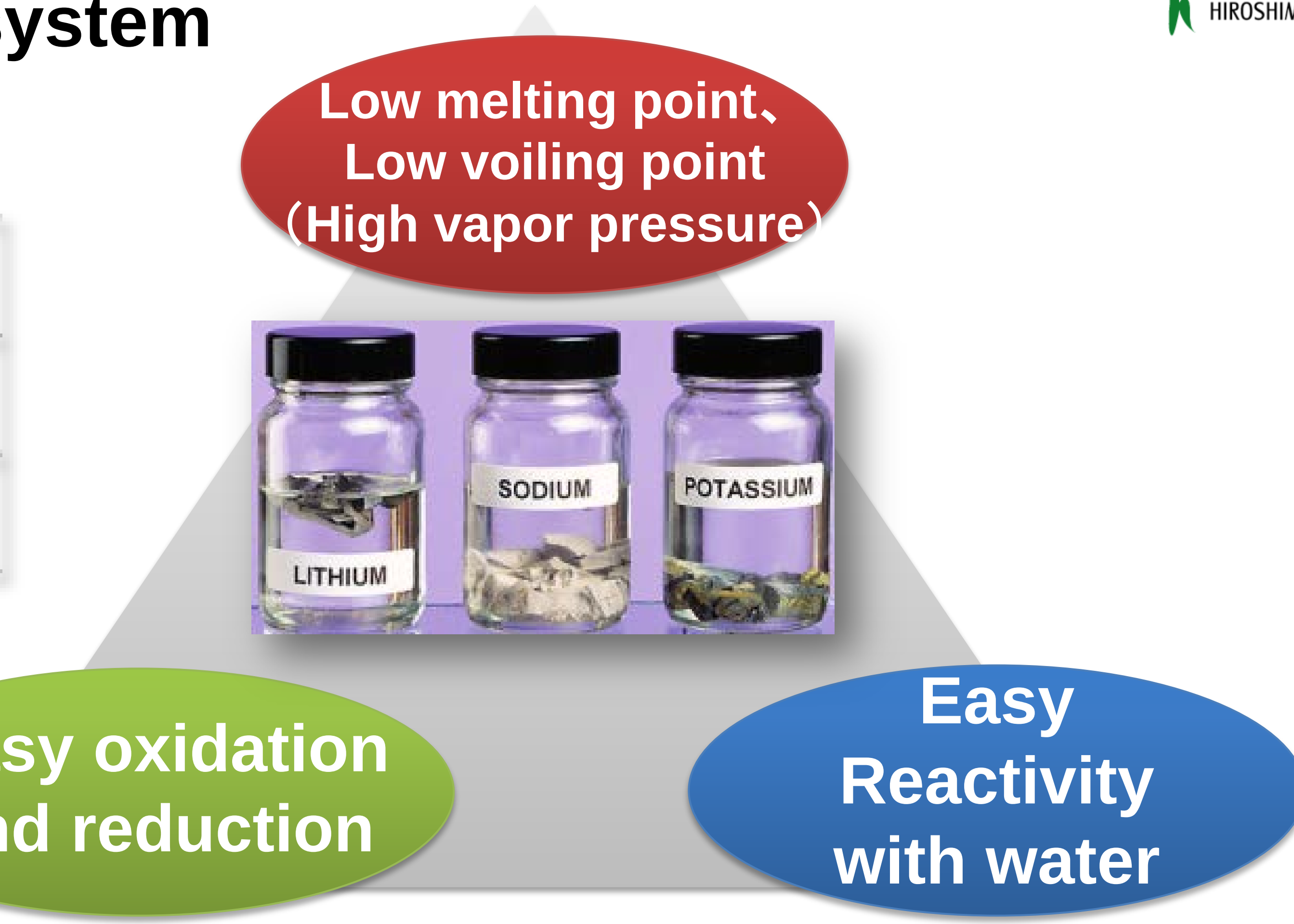
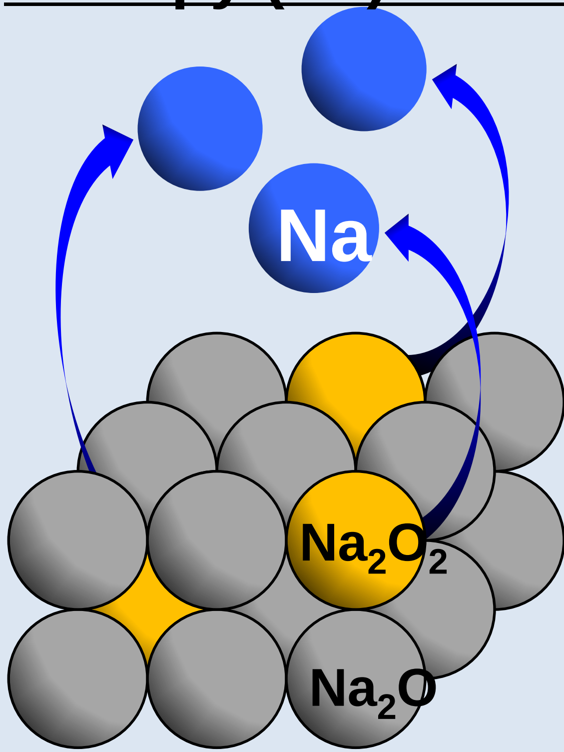


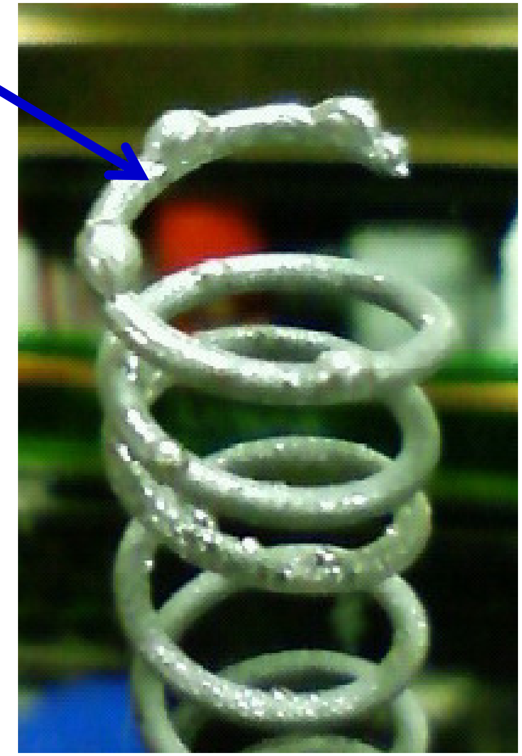
The possibility of H_2 production below 500 °C by water-splitting via reactions of the Na Redox system was experimentally demonstrated.

H. Miyaoka, T. Ichikawa, N. Nakamura, Y. Kojima, Int. J. Hydrogen Energy, 37, 17709-17714 (2012)

Entropy (ΔS) control



Na metal



$$2Na_2O \rightarrow Na_2O_2 + 2Na(g) \quad 500°C$$

$$Na_2O_2 + H_2O(l) \rightarrow 2NaOH + 1/2O_2 \quad 100\ °C$$

$$2NaOH + 2Na(l) \rightarrow 2Na_2O + H_2 \quad 350\ °C$$

Haber-Bosch process

4.2 NH_3 utilization

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

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

Driving range: 700km
Filling time: 3 minutes

Driving range: 800km
Filling time: 3minutes

140-160km/kgH_2

Hydrogen price: barrier to the popularization

NH_3 decomposition and removal technology to produce H_2

NH_3 decomposition technology

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Catalytic activity

Cartalyst	Conversion /%		
	673K	773K	873K
Ru/CNT-KNO_3 Ru-KNO_3/MgO-CNTs	50 80	–	–
Ru/LSZ-DP 30000 $mLg^{-1}h^{-1}$ Ru/LSZ-DP 4000 $mLg^{-1}h^{-1}$	18 54	75 100	100 100
10%Ru/SiO_2	14.3	64.0	97
Ru/Cs_2O/Pr_6O_{11}	99.6 93(623K)	99.9	>99.9
Nano-Ru/SiO_2	34	90	100
Nano-Ni/SiO_2	8.5	35	82
Nano-Fe/meso SiO_2	7	27	86
Ni/Al_2O_3 Ni/La_2O_3	5 6	34 33	97 90
Fe_2O_3/CMK-5 NiO/Al_2O_3	9(723) 6(723)	26 17	96 80
Nano-Ni/Zeolite(1h)	–	22	–

550℃
800ppm

ISO14687-2

Ammonia concentration: <0.1ppm

1. Alkali metal hydride-NH_3 system(reaction)
2. Metal ammine complex (absorption)
3. Adsorbent
4. Separation membrane

LSZ: Lanthanum-stabilized zirconia,
CMK-5: Ordered mesoporous carbon

NH_3 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.)

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

4. Summary

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 H_2 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.

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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.

Acknowledgement: This work was partially supported by Council for Science, Technology and Innovation(CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "energy carrier"(Funding agency : JST).」