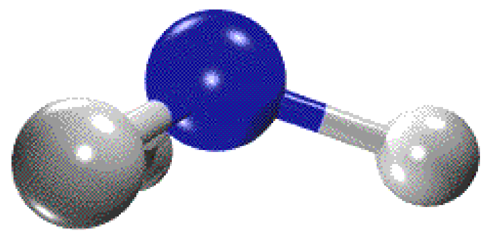
Cross-ministerial Strategic Innovation
Promotion Program (SIP)

Ammonia Storage Materials Using Metal Halides and Borohydrides



NH_3 Fuel Conference 2016

September 18-21, 2016, Los Angeles, CA

(9:05-9:30, September 20, 2016)

Yoshitsugu Kojima

Hiroshima University

Institute for Advanced Materials Research

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Itsukushima Shinto Shrine

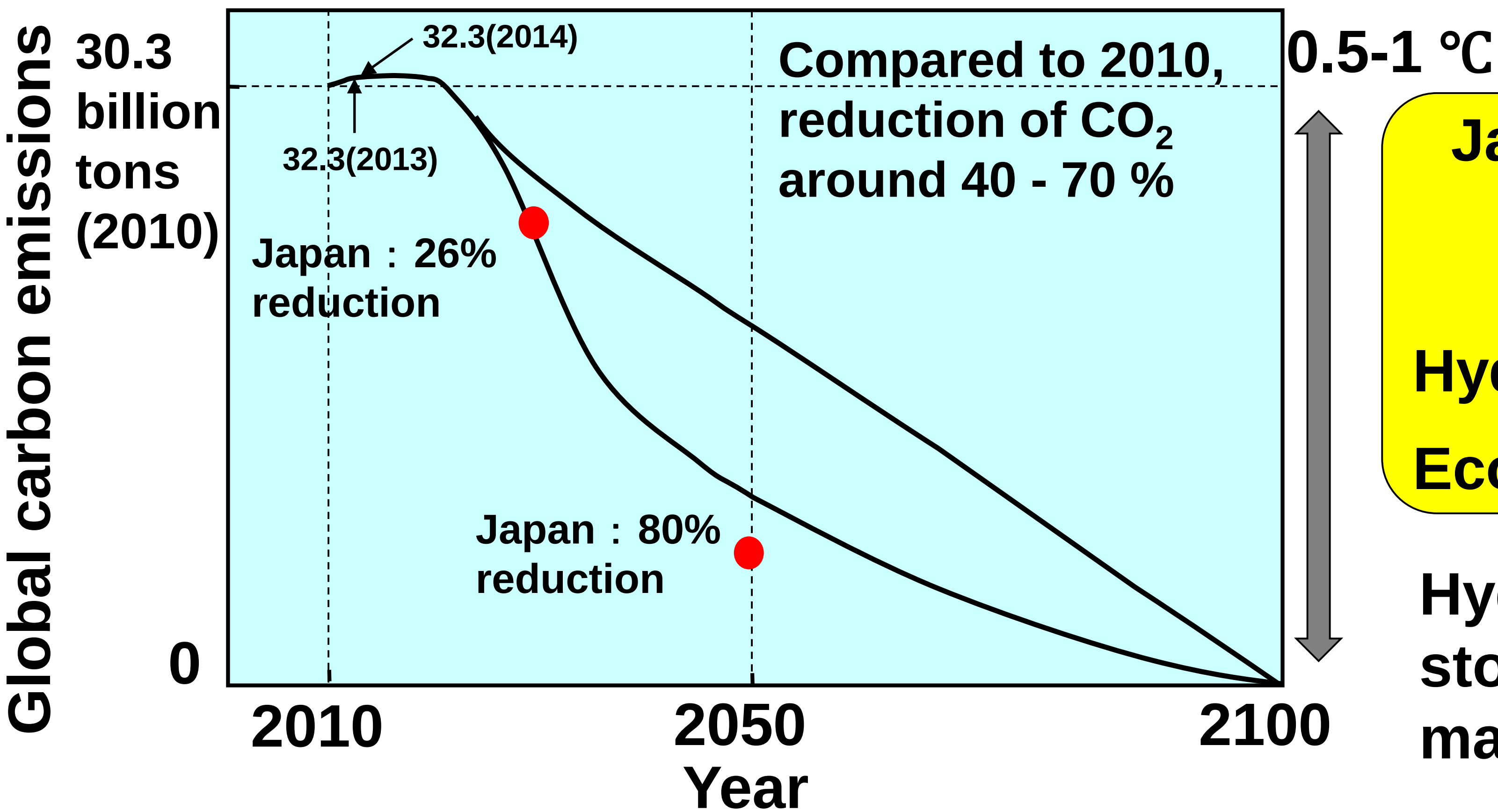
Hiroshima Peace Memorial

1. Energy and Environmental Issues

(1) We have a transportation liquid fuel crisis.
(70% of world energy cash flow is around oil.)

(2) Negative effects of global warming
(sea level rise, abnormal weather etc.)

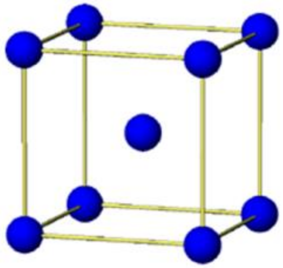
Global carbon emissions pathways reported by IPCC and COP21



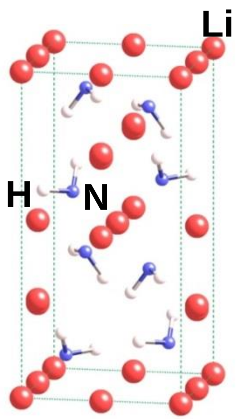
Japan
↓
Hydrogen Economy

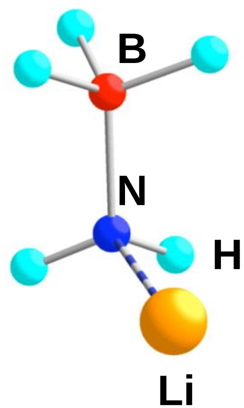
Hydrogen storage materials

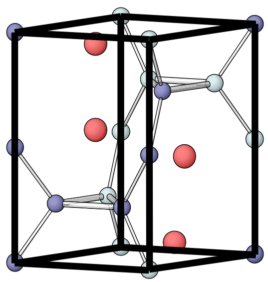
2. Research on hydrogen carrier (hydrogen storage materials) (1999-2016)



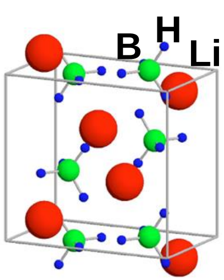
BCC



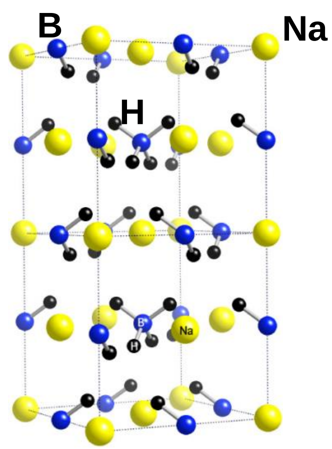




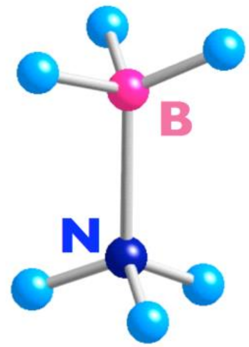
AB2

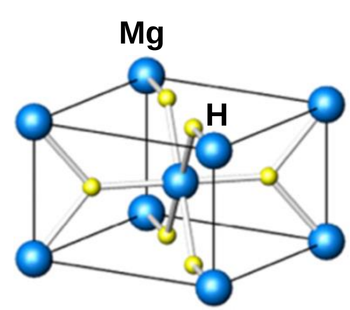


Hydrogen absorbing alloy

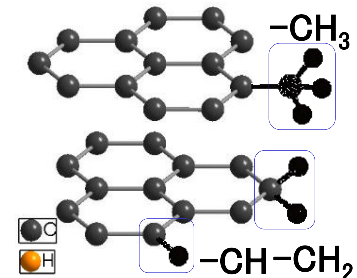


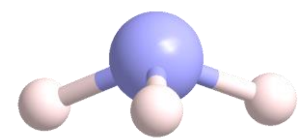
Complex hydrides

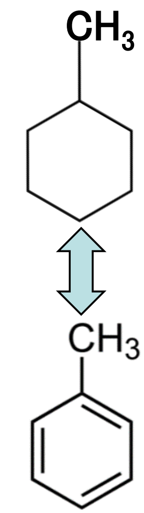




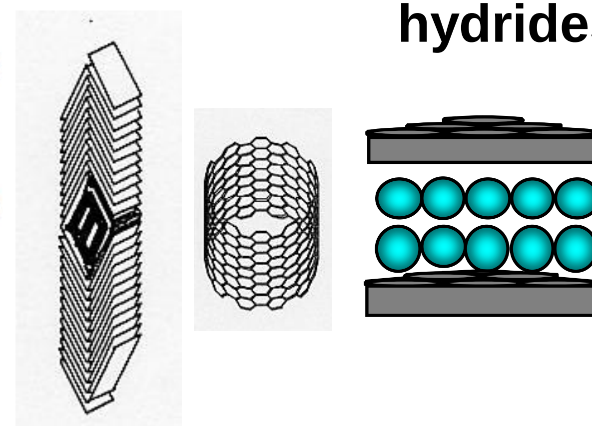
Inorganic hydrides







Organic hydrides



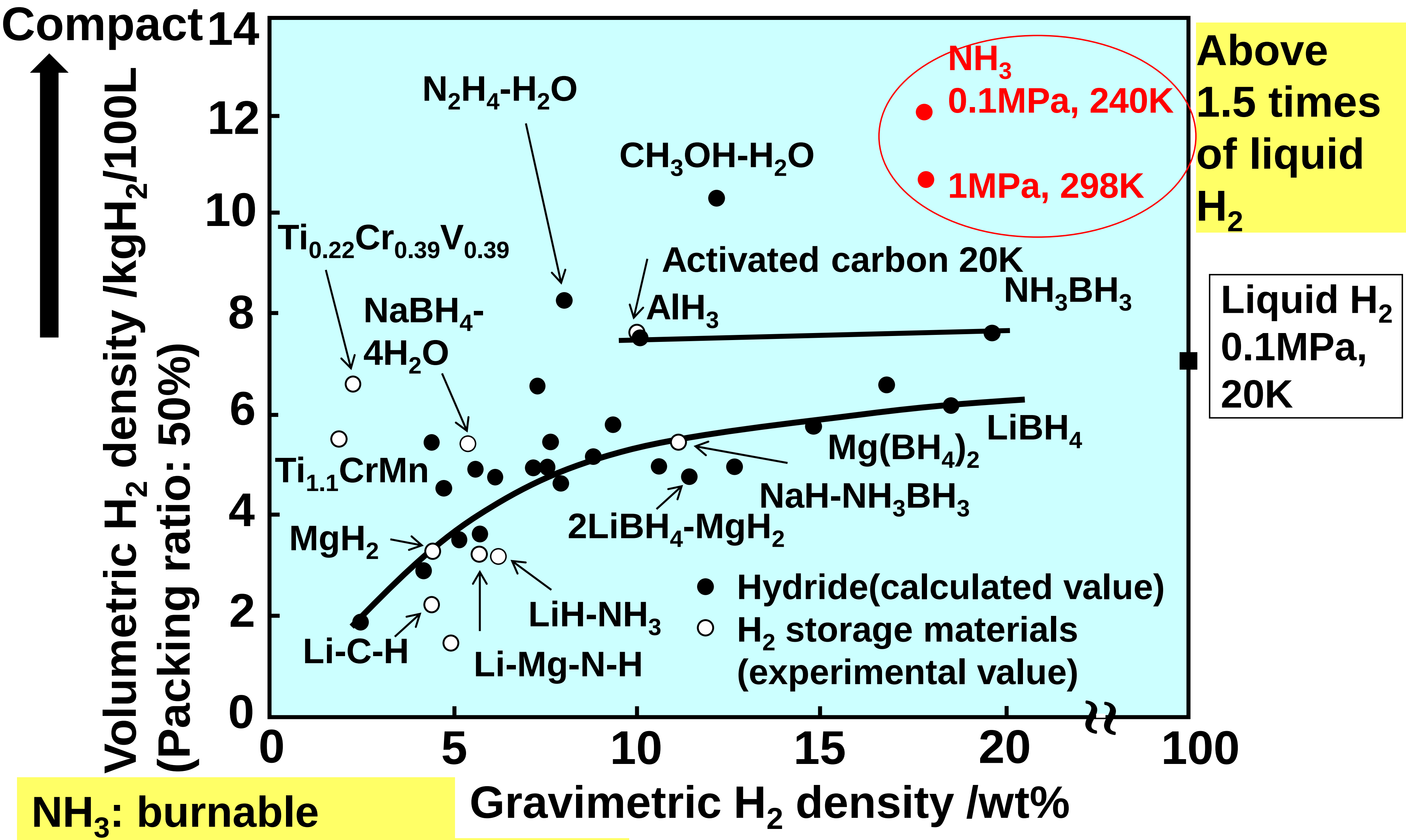
Carbon materials

Evaluation and characterization of 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.

3. Properties and Safety of Ammonia

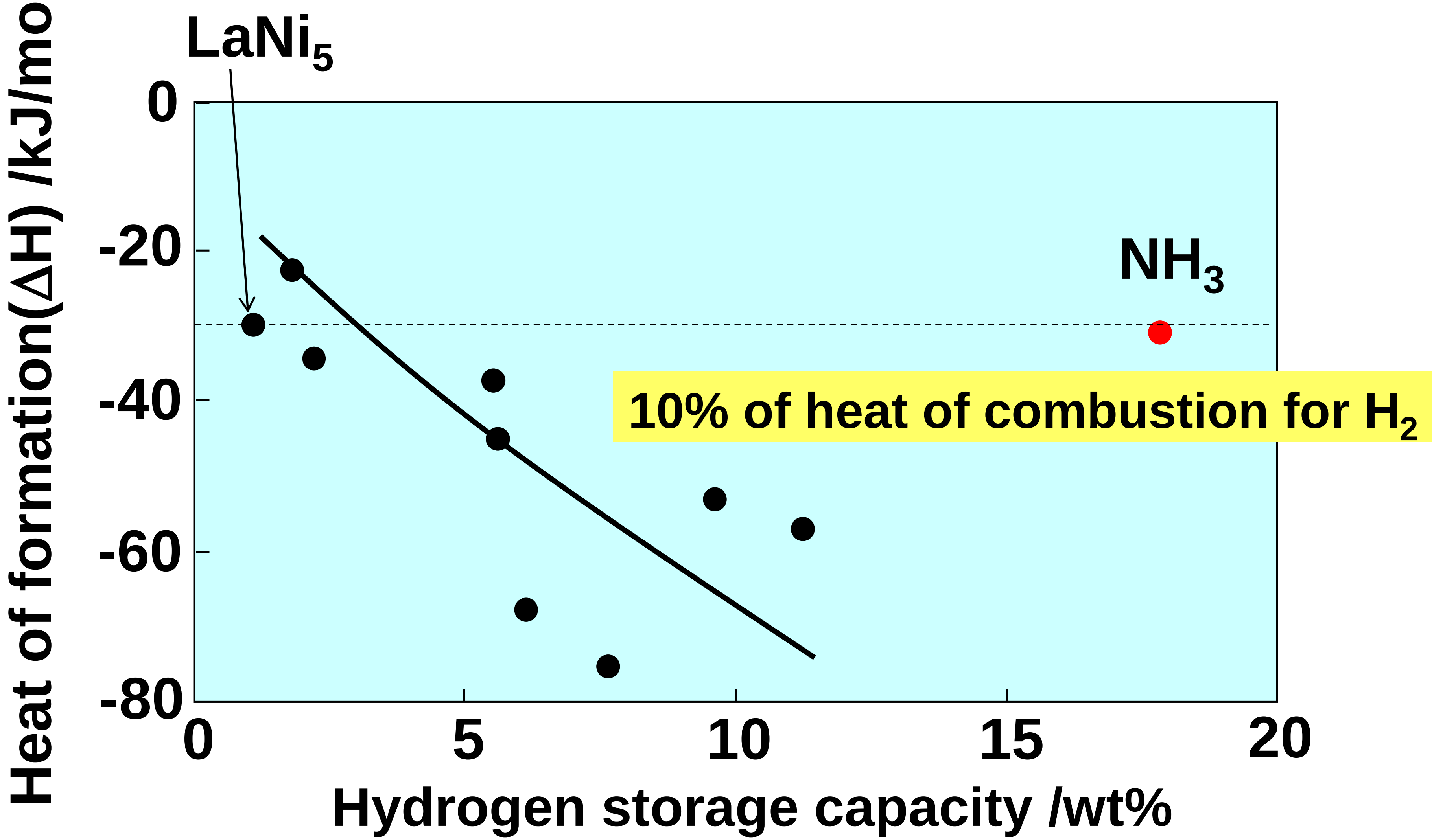
H_2 densities of hydrogen carrier(solid, liquid)



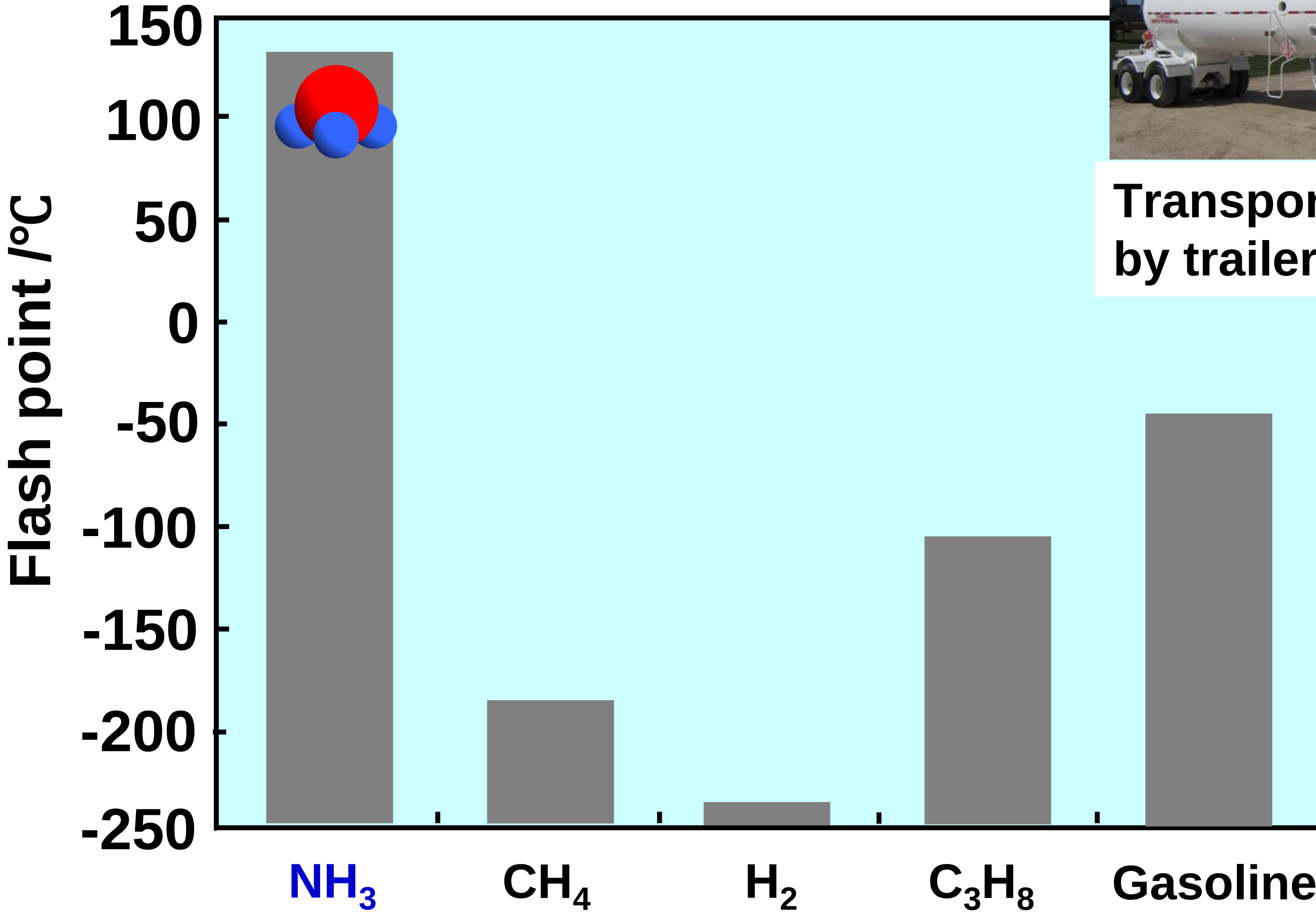
Above 1.5 times of liquid H_2

NH_3: burnable substance → Energy carrier

Heat of formation and H_2 storage capacity of hydrogen storage materials



Flammability of ammonia and transportation fuel



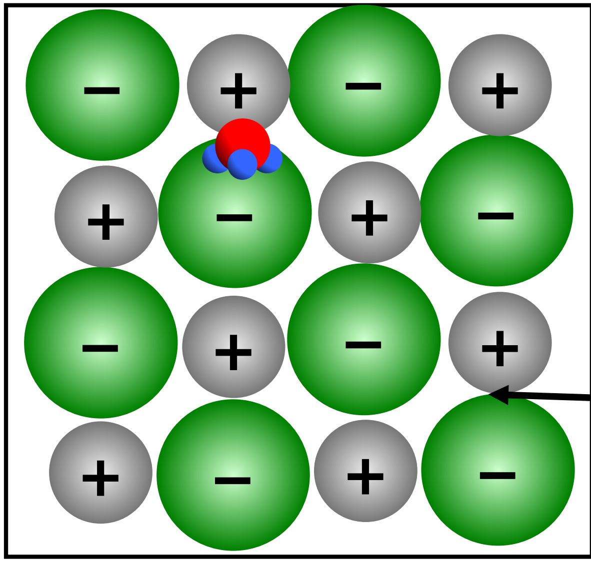
Transportation 26 tons by trailer (H_2: 4.6 tons)

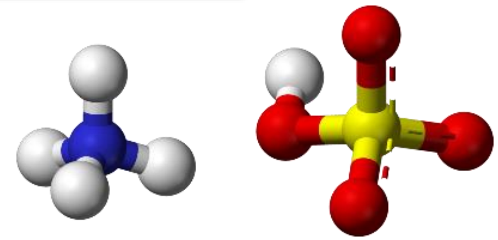
To improve health hazard, vapor pressure

Ammonia concentration 100% → deleterious substance

4. Ammonia Storage Materials

Materials having ionic bond





Bonding State(electronegativity) vs. vapor pressure

Metal Halides
LiCl, LiF
LiI, NaCl
NaI, $MgCl_2$
$CaCl_2$, NiI_2 etc.

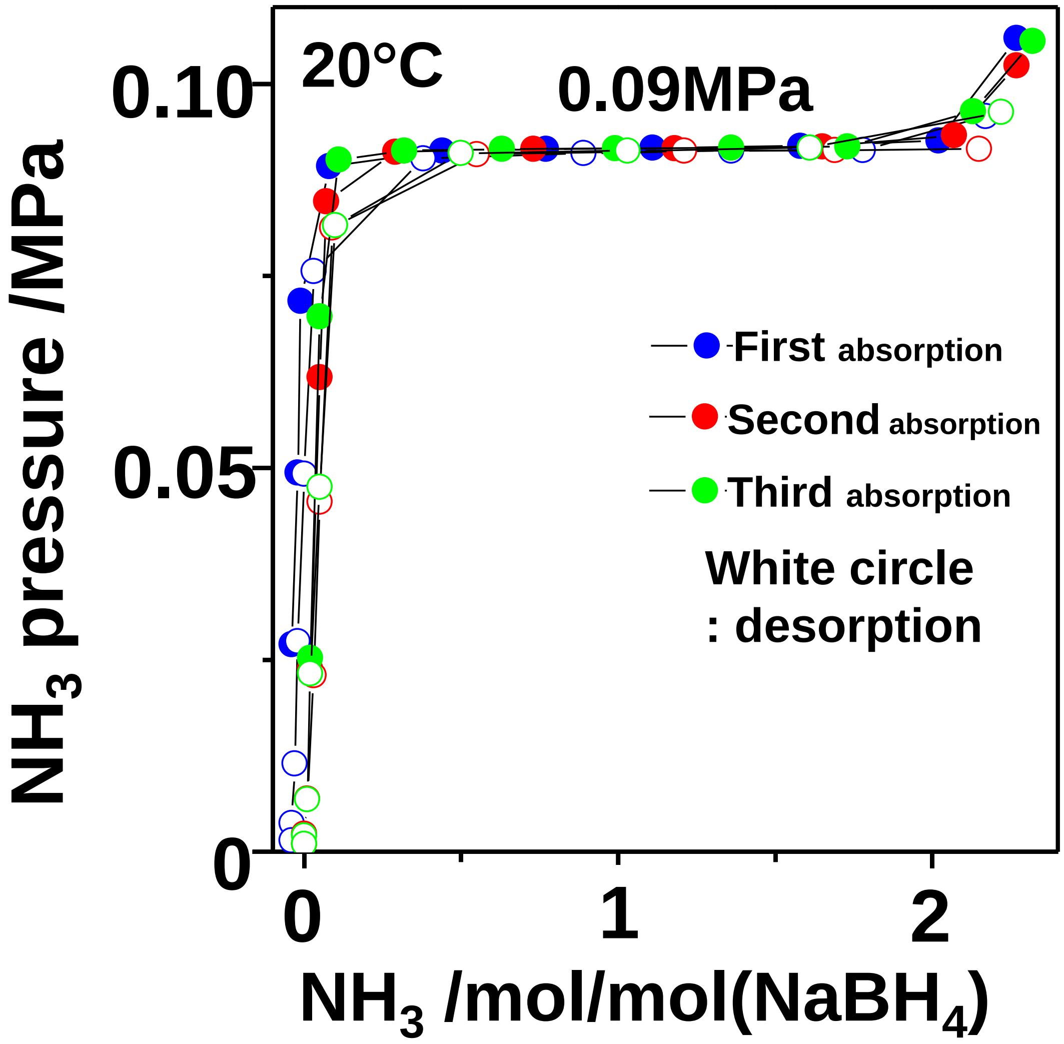
Borohydrides
$LiBH_4$, $NaBH_4$
KBH_4, $Mg(BH_4)_2$
$Ca(BH_4)_2$, etc.

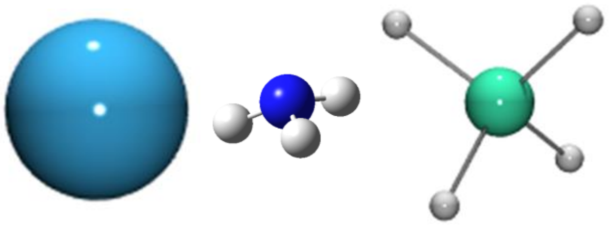
Ammonium Hydrogen Sulfate

NH_4HSO_4

Purpose: Relationship among NH_3 pressure, electronegativities of cation and anion

P-C isotherm for $NaBH_4$-NH_3 system



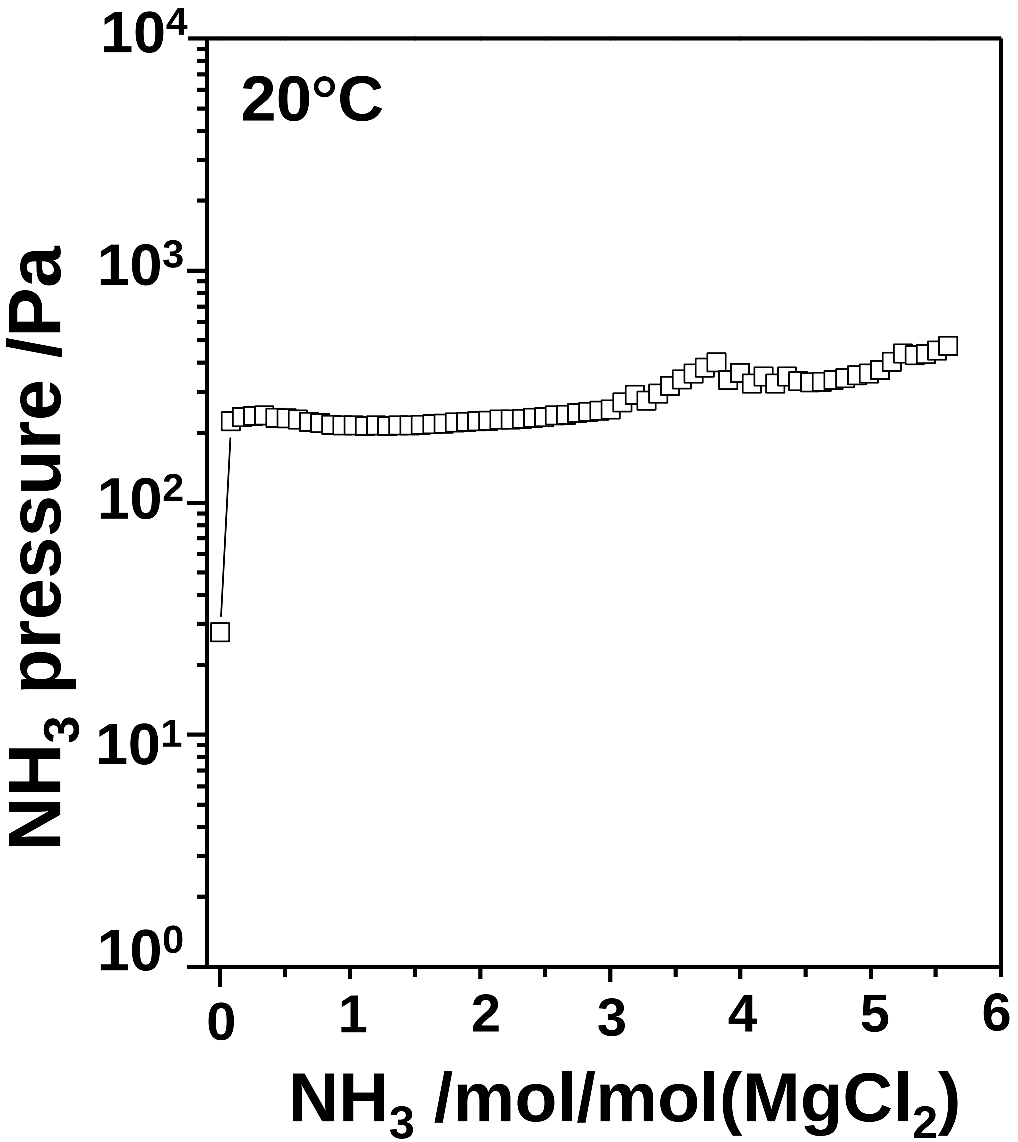


1-2mol/mol,
0.09MPa

1/10

NH_3 vapor pressure of $NaBH_4$(0.09MPa) < NH_3 vapor pressure (0.86MPa)

P-C isotherm for $MgCl_2$-NH_3 system

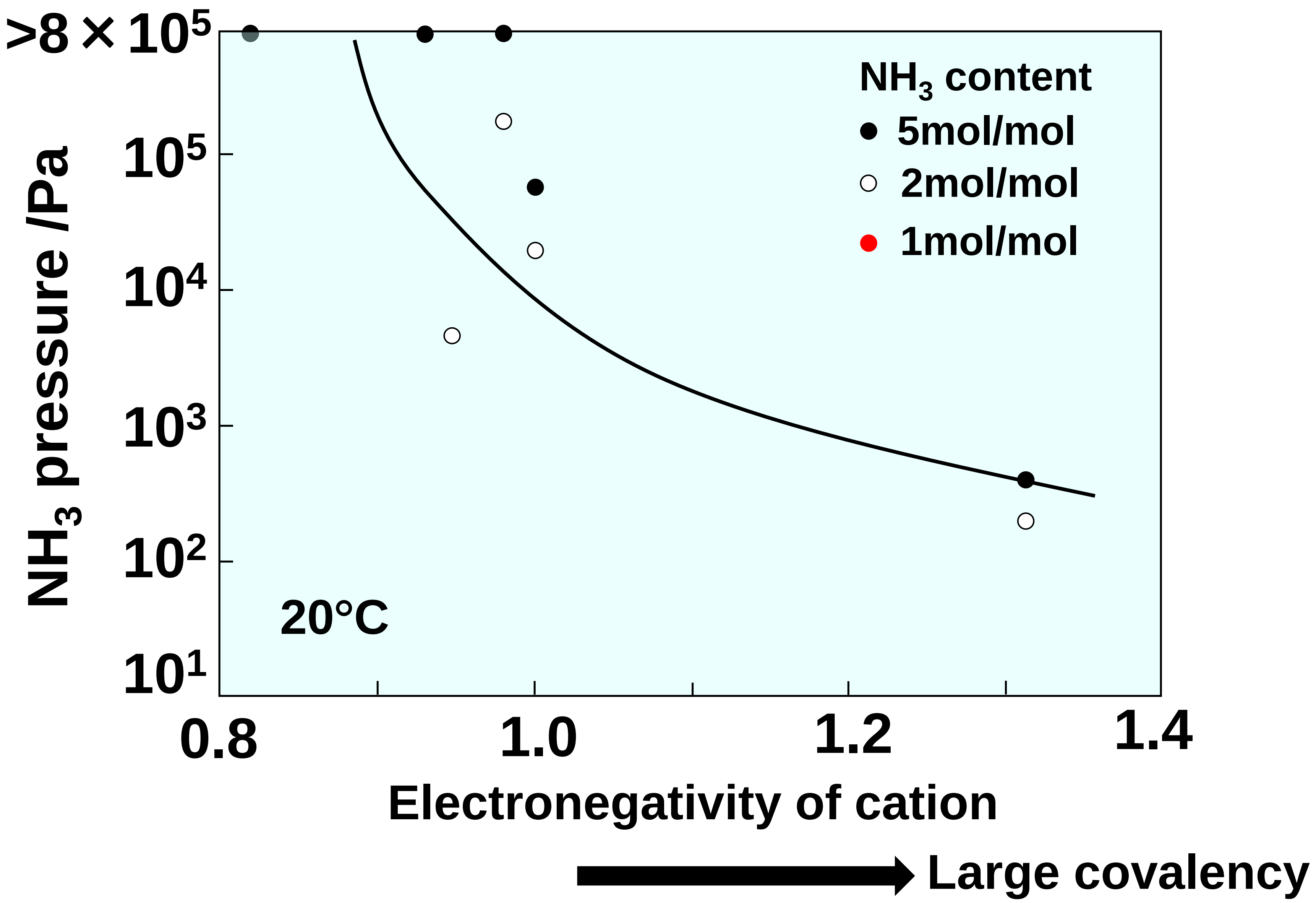


1-5mol/mol,
200-400Pa
(2000-4000ppm)

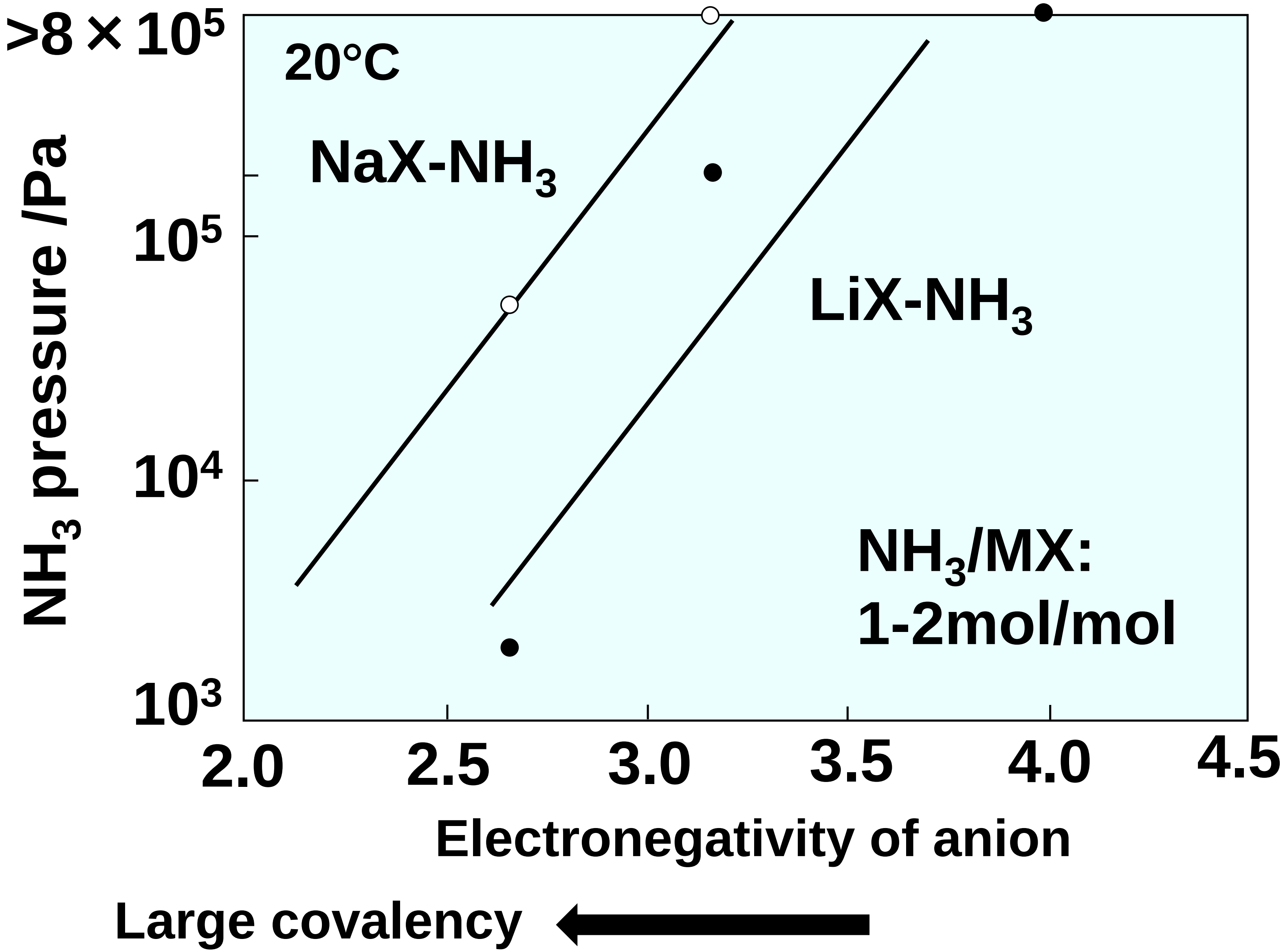
1/3000

NH_3 vapor pressure of $MgCl_2$ < NH_3 vapor pressure (0.86MPa)

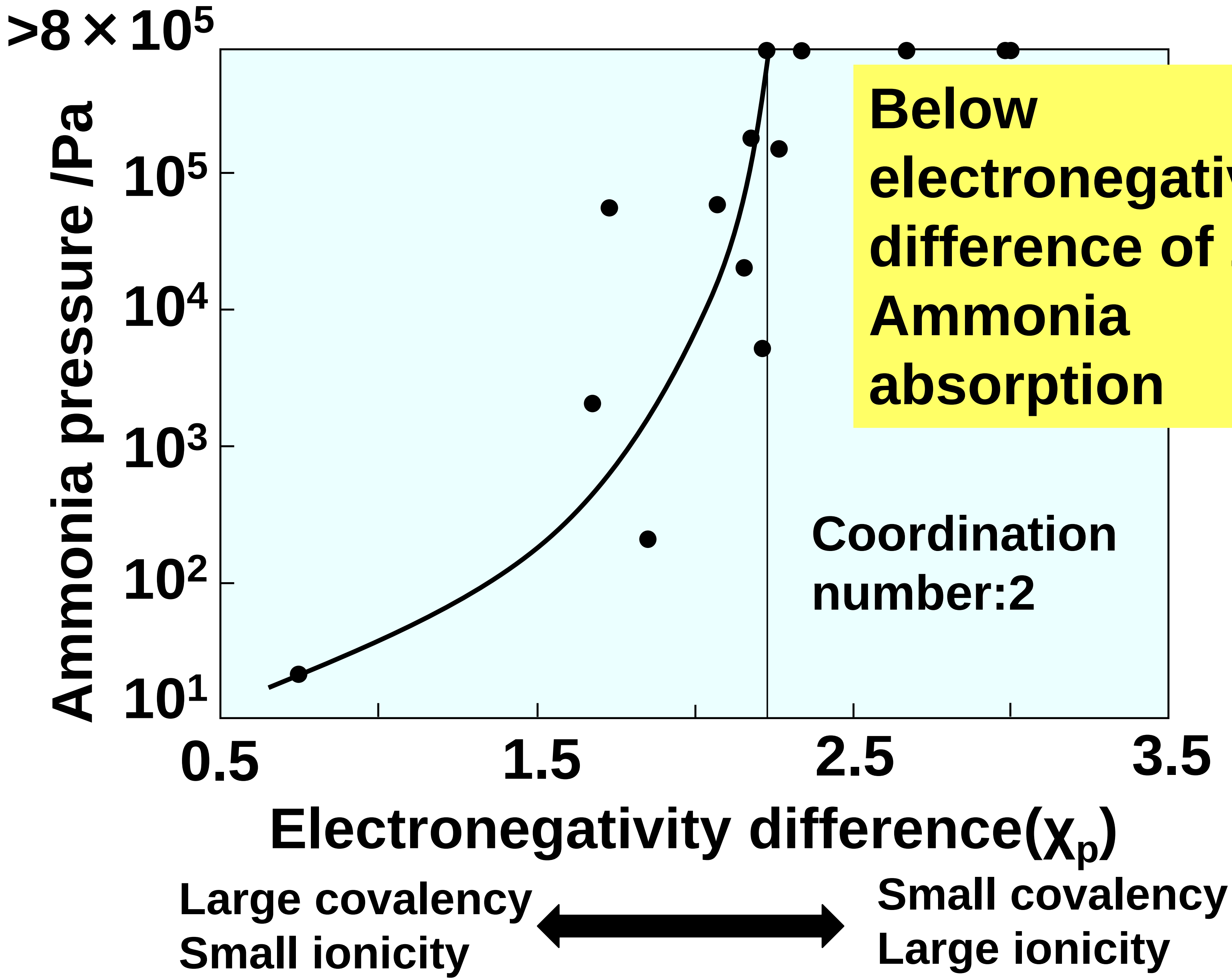
Relation between NH_3 pressure of chloride-NH_3 system and electronegativity of cation



Relation between NH_3 pressure of halide MX-NH_3 (M: Na, Li, X: F, Cl, I) system and electronegativity of anion



NH_3 pressure as a function of electronegativity difference



Ammonium Hydrogen Sulfate

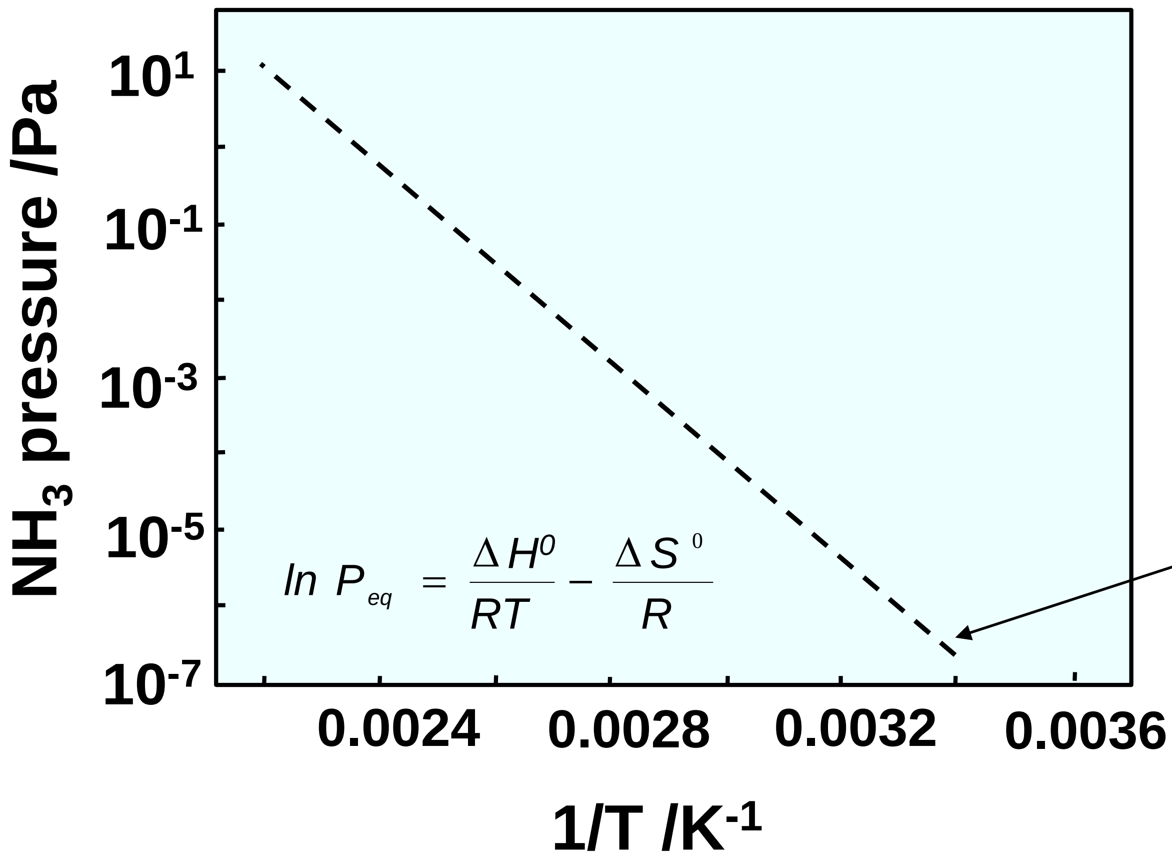
$$NH_4HSO_4 + NH_3 \leftrightarrow (NH_4)_2SO_4$$

Standard enthalpy change -108kJ/molNH_3

Standard entropy change -198J/molK (entropy of NH_3: 193J/molK)

W. D. Scott, F.C. R. Cattell, Atmospheric Environment, 13, 307-317 (1979)

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



Below 10^{-6}Pa (20°C,10^{-5}ppm)

Below 0.1ppm (0.01Pa)

5. Hydrogen production for fuel cell vehicles

Specification of hydrogen fuel for FCV (ISO 14687-2:2012)

Species	Concentration
Purity of H_2	99.97%
Total hydrocarbons(C1)	2ppm
Water(H_2O)	5ppm
Oxygen(O_2)	5ppm
N_2, Ar	100ppm
He	300ppm
Carbon Dioxide(CO_2)	2ppm
Carbon Monoxide(CO)	0.2ppm
Total sulphur compounds	0.004ppm
Formaldehyde	0.01ppm
Formic acid	0.2ppm
Ammonia	0.1ppm
Total halogenated compounds	0.05ppm

NH_3 remover

⬆

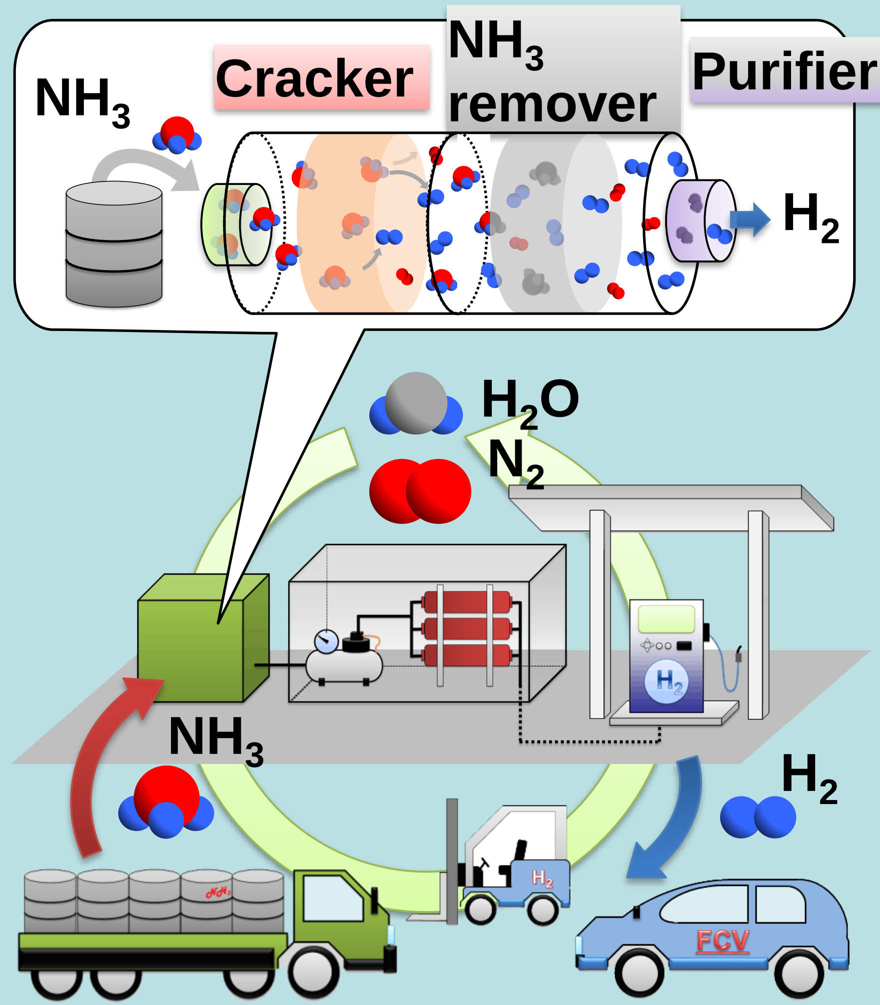
Application of NH_3 storage materials

Press release
July 19, 2016

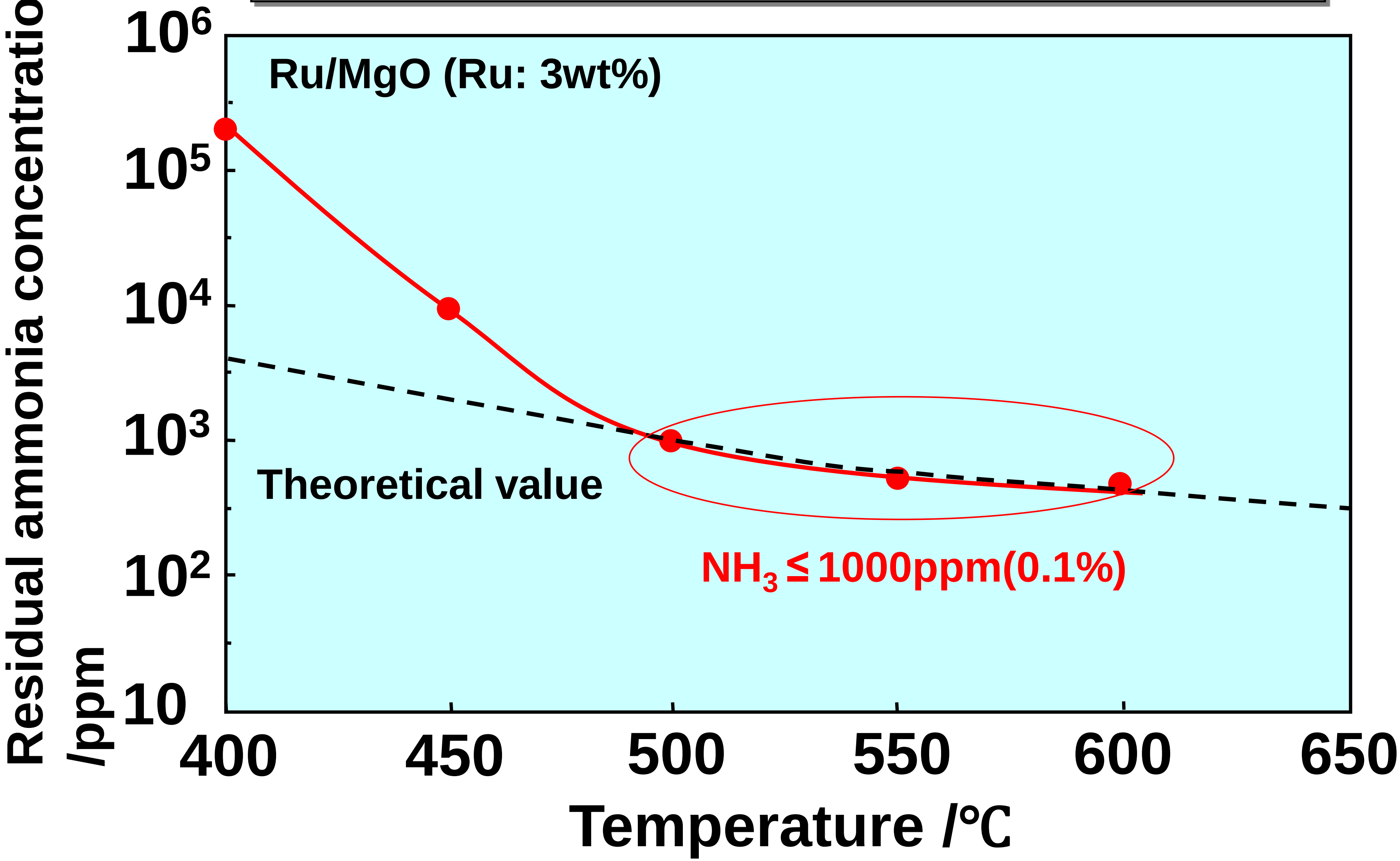
Hydrogen production for fuel cell vehicles from ammonia

Hiroshima University, Showa Denko, Taiyo Nippon Sanso, National Institute of Advanced Industrial Science and Technology (AIST), and Toyota Industries developed technologies to produce high-purity hydrogen to meet ISO14687-2 (NH_3 ≤0.1ppm, N_2 ≤1ppm, H_2 ≥99.97%) from ammonia for the first time in the world.

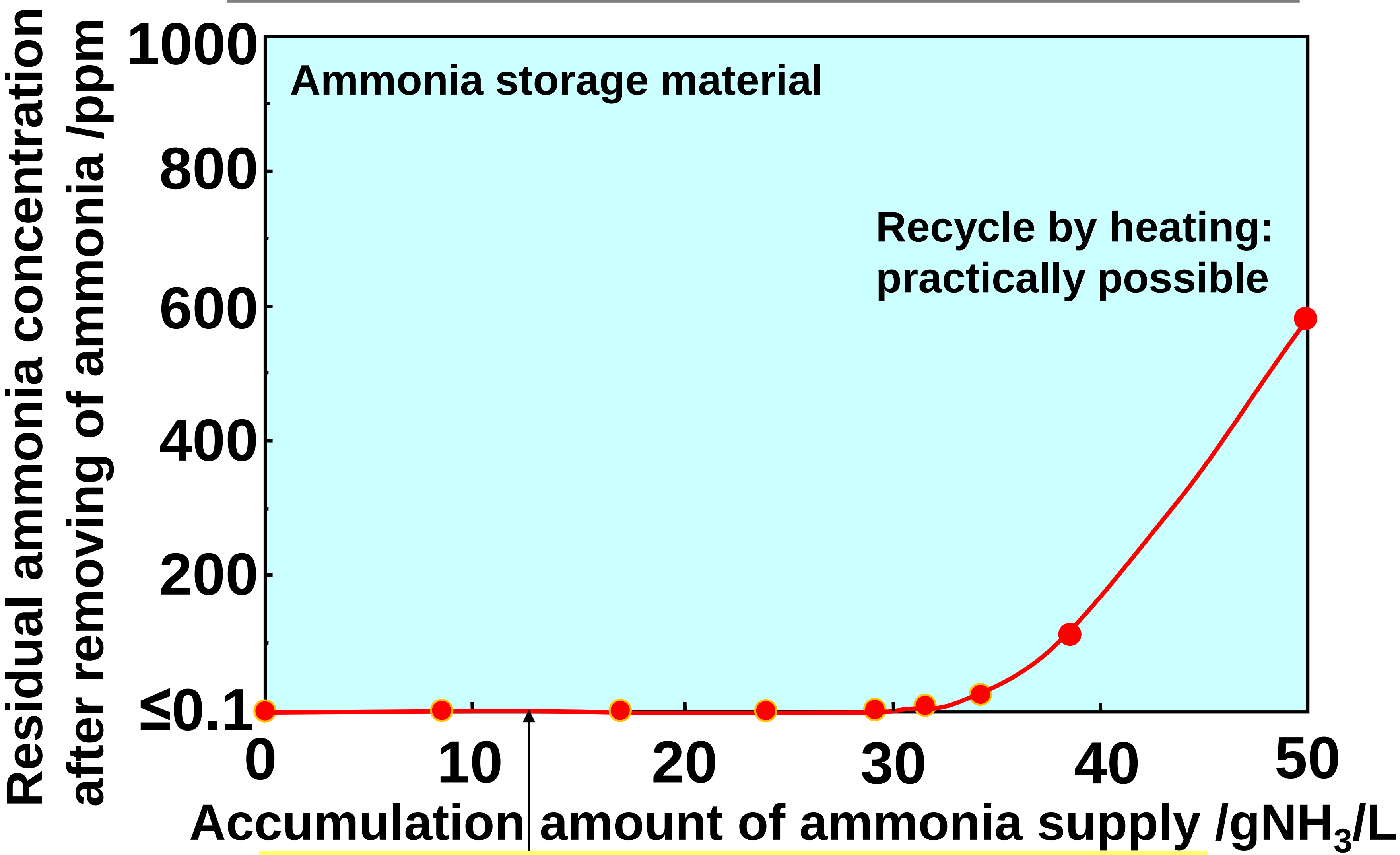
Ammonia decomposition and high purity H_2 supply system



Comparison of ammonia concentration as a function of reaction temperature



Residual ammonia concentration after removing of ammonia



Ammonia elimination quantity: 30gNH_3/L (long optical path length IR)

SHOWA DENKO TOYOTA TAIYO NIPPON SANSO

Ammonia decomposition and high purity H_2 supply system ($1Nm^3/h$)

Ru/MgO catalyst

Ammonia storage material

NH_3

$1Nm^3$ /h

H_2

about $1Nm^3$ /h

NH_3 Cracker and remover

H_2 purifier

Future plan: system demonstration

6. Summary

1. **Ammonia pressure decreases with the electronegativity of cation and decrease in the electronegativity of anion.**
2. **Ammonia pressure increases with the electronegativity difference below the value of 2.2.**
3. **High purity hydrogen gas was produced by Ru-based catalyst, ammonia storage material and purification method.**

Acknowledgement

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

The 8th World Hydrogen Technologies Convention in 2019 (WHTC 2019), Tokyo

June 2(Sunday)-7(Friday) Tokyo International Forum
Chair: H. Kameyama
Vice Chairs: Y. Kojima, N. Kuriyama, S. Mitsushima, K. Sakata, H. Uchida
Secretary General: H. Takagi

Hosted by Hydrogen Energy Systems Society of Japan (HESS)

Tokyo International Forum

Supported by International Association for Hydrogen Energy (IAHE)

Thank you for your attention.