NH_3 as a Hydrogen Career

1-2 of October 2012

9th Annual NH_3 Fuel Association Conference

Yoshitsugu Kojima
Hiroshima University
Institute for Advanced Materials Research

Table of Contents

1. Energy and Environmental Issues
2. Research on Hydrogen Storage Materials
3. Characteristics of NH_3
4. NH_3 utilization
5. Future perspective
6. Summary

Itsukushima Shinto Shrine

Hiroshima Peace Memorial

1. Energy and Environmental Issues

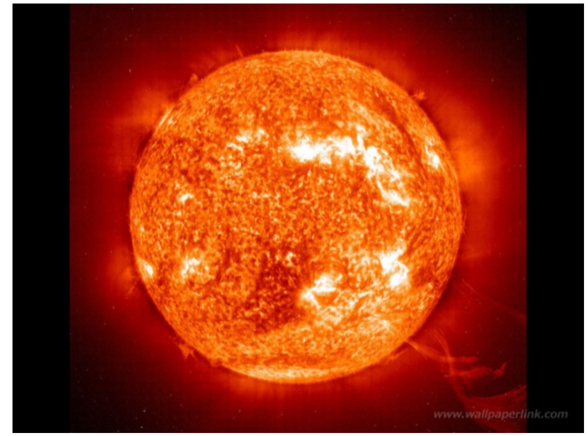
History of Industrial Revolution

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

Sustainable economy

12 billion ton of oil equivalent

Secondary energy →H_2

2. Research on Hydrogen Storage Materials

Hydrogen career ?

⬇

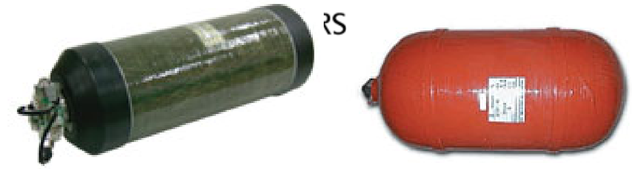
Liquid hydrogen

Liquid hydrogen(20K) , 7kgH_2/100L

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, 3.9kgH_2

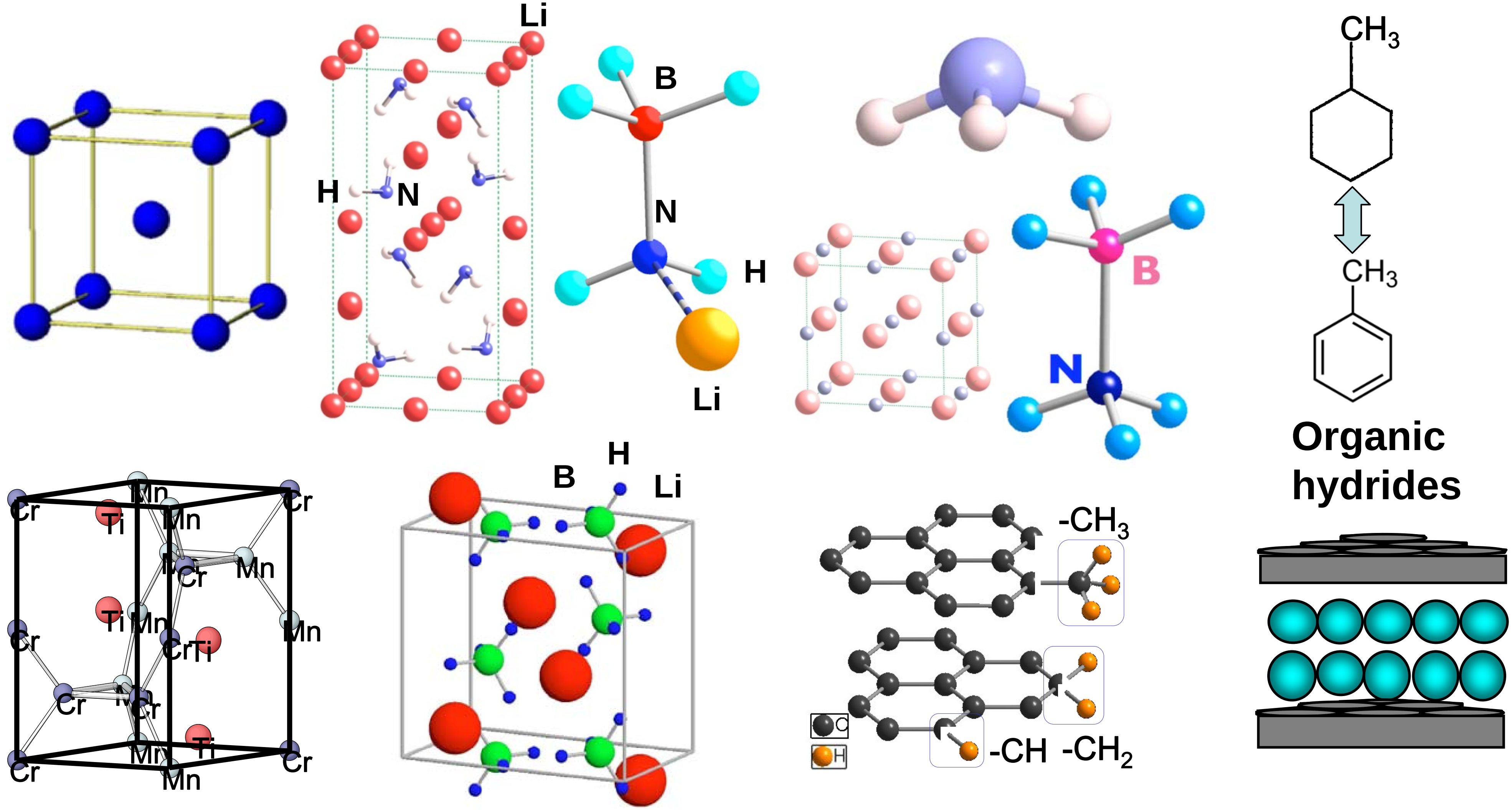
Internal volume: 156L, 6.1kgH_2

130-160km/1kgH_2

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

Hydrogen storage materials

Hydrogen storage materials (1999 ~ 2012)



Organic hydrides

Hydrogen absorbing alloy

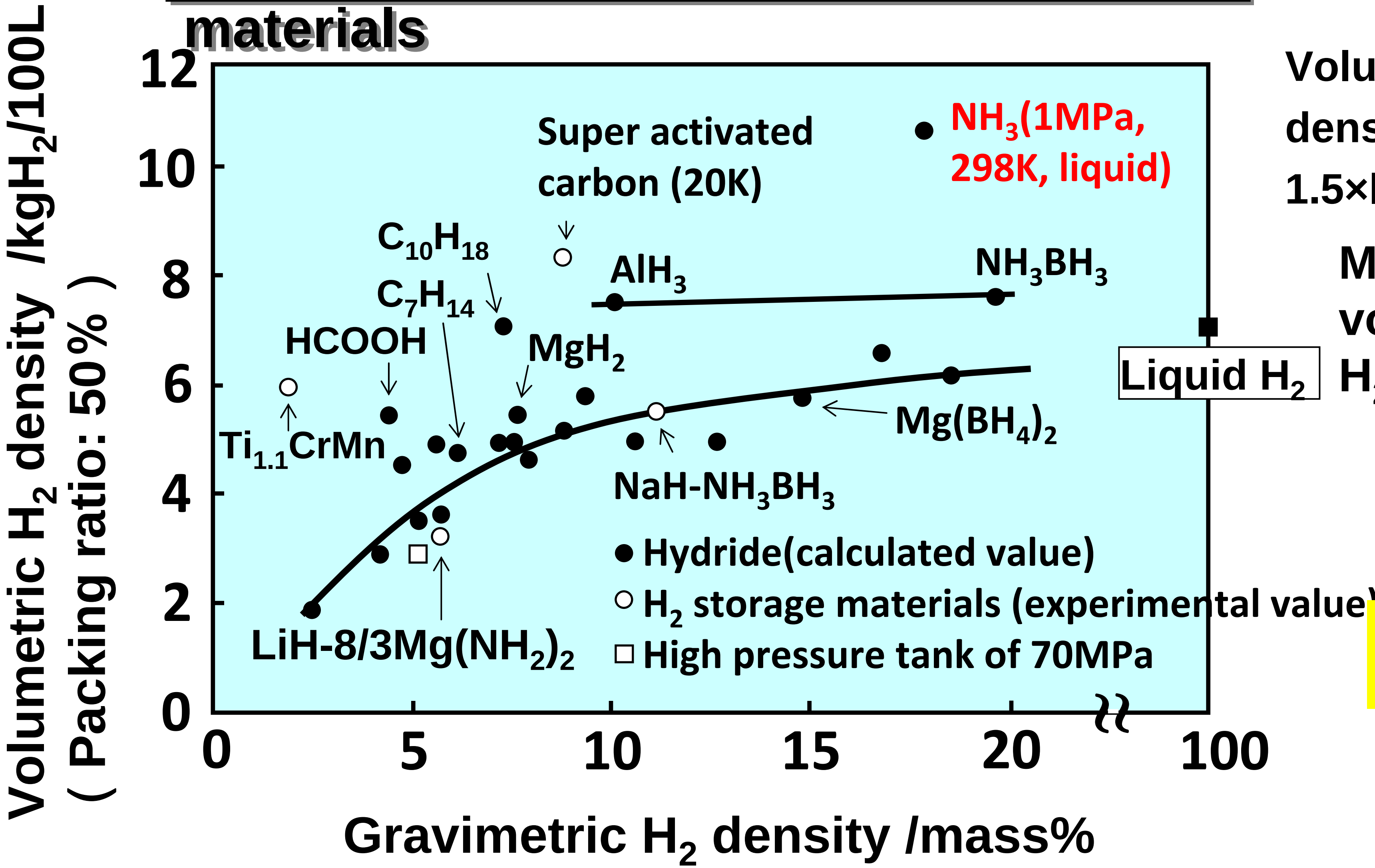
Complex hydrides

Inorganic hydrides

Porous materials

Evaluation and characterization of 200 kinds of hydrogen storage

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

NH_3

3. Characteristics of NH_3

Haber-Bosch process

10-25MPa, 573-823K

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

Annual production of the world 153 million ton (2008)

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

NH_3: Inclusion of hydrogen

Renewable fuel independent of fossil fuel

NH_3
0.18kgH_2/kg material
0.107kgH_2/L material

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

Table 2 Technical Targets: Onboard Hydrogen Storage Systems

Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass) [a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost [b]:	\$/kWh net (\$/kg H_2)	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost [c]	\$/gge at pump	3-7	2-4	2-4

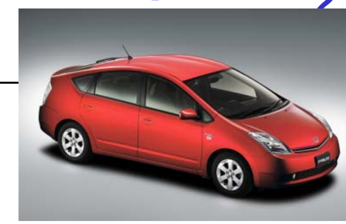
\$2-4/gge
（2010～2011)

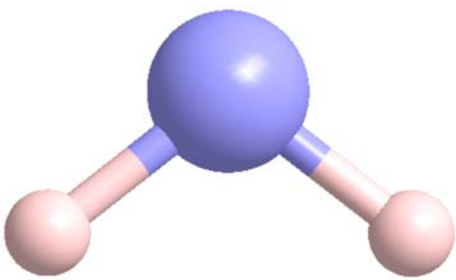
Gasoline gallon equivalent

H/M:2,H_2:11mass%
ΔH: -285kJ/molH_2

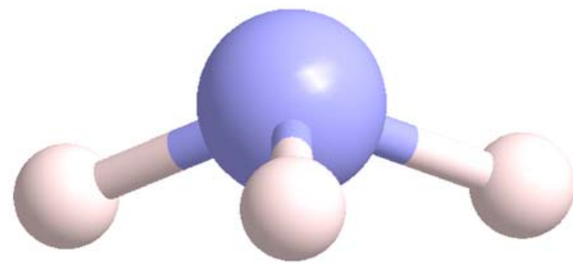
H/M: 3,H_2:18mass%
ΔH: -31kJ/molH_2

Specimen	$Mg(BH_4)_2$	NH_3	H_2 absorbing alloy ($LaNi_5$)
H_2 content ΔH	15mass% -57 ~ -75kJ/molH_2	18mass% -31kJ/molH_2	1.5mass% -31kJ/molH_2



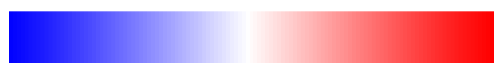


H_2O



NH_3

Partial atomic charges



Stable under water and oxygen

"Safety Assessment of Ammonia as a Transport Fuel"

Risø National Laboratory, Denmark (2005)

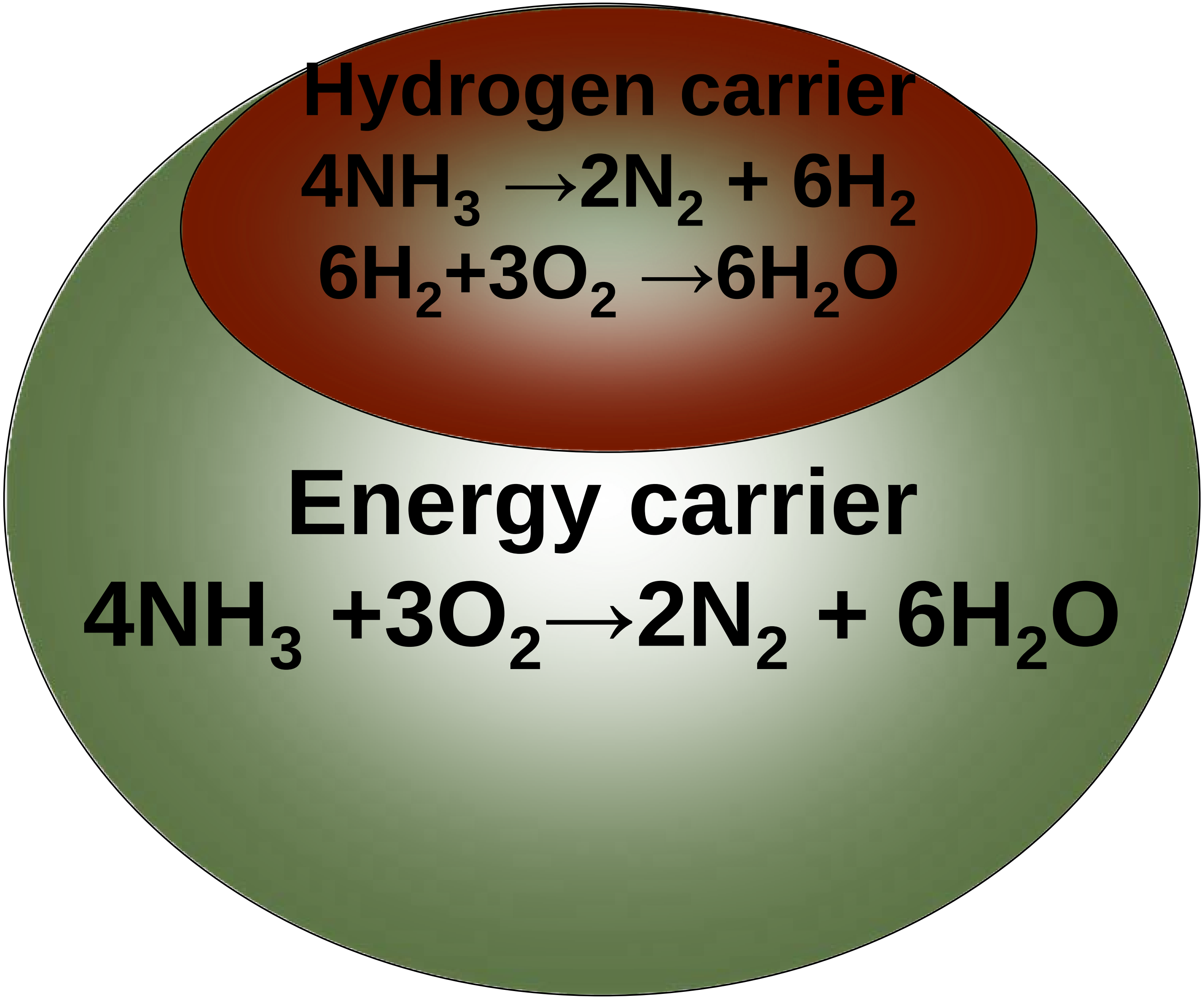
Substance		Health	Flammability	Flash point
Ammonia	GWP: 0	3	1	132
Natural gas	GWP: 21	1	4	-187
Methane	GWP: 21	1	4	-187
Hydrogen	GWP: 0	0	4	-157
LPG(propane)		1	4	-104
Methanol		1	3	60.4
Gasoline(92 octane)		1	3	-43

GWP: Global warming potential

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. NH_3 utilization



NH_3

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)

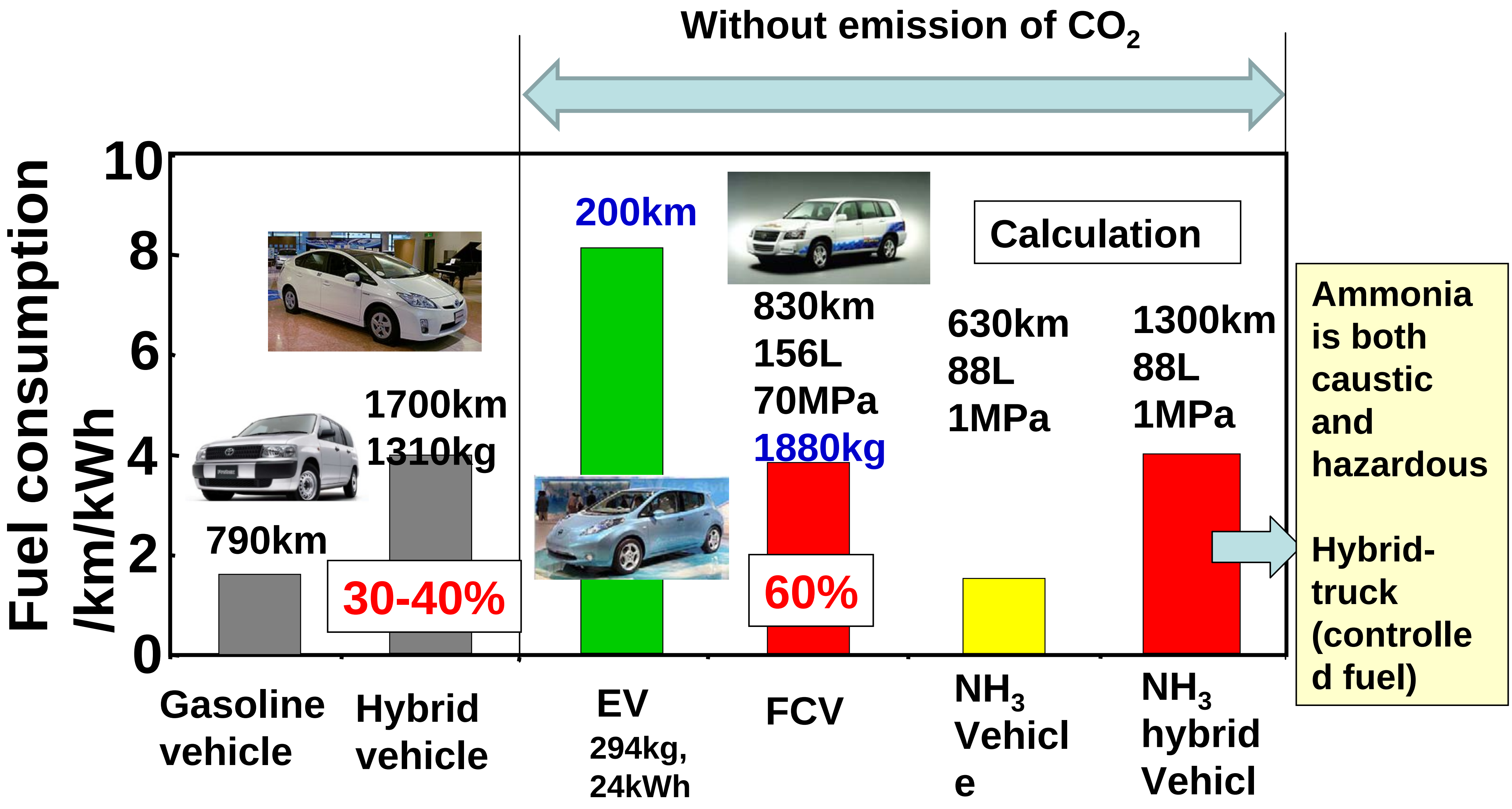
Item		Liquid H_2 system	NH_3 system
Input electric energy		100	100
Energy after production		72.9	70.3
Energy loss by transportation (5000km)		(2.5)	(1.6)
Energy after transportation		70.4	68.7
Plant cost /million dollars		7400	5400
Energy generated (Efficiency: 60%) Combined Cycle	hydrogen carrier	42 H_2 gas turbine (100-300MW)	32 H_2 gas turbine
	energy carrier		41 NH_3 gas turbine

NH_3 SOFC 1kW-1MW

Efficiency: 60%

http://www.enaa.or.jp/WE-NET/report/1996/japanese/3_1.html

Fuel consumption of next generation vehicle



Fuel consumption ∝ Tank to wheel ∝ efficiency

4.3 Energy and hydrogen career

HIROSHIMA UNIVERSITY IAMR HiH2

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 H_2 and NH_3, generation of high purity H_2) , Cold start
2. Ammonia storage materials (lower vapor pressure), Harmless NH_3

(1) Conversion from ammonia to hydrogen at RT

MH-NH_3

523-573K, 0.5MPa, H_2 flow

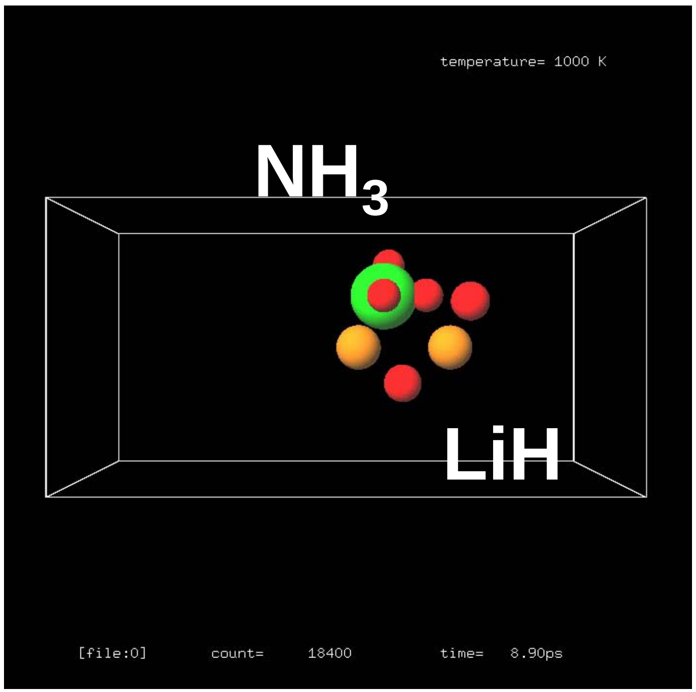
$$LiH + NH_3 \rightarrow LiNH_2 + H_2 \quad (1)$$

ΔH^0: -43kJ/molH_2 H_2 content:8.1mass%

H_2 generation at room temperature

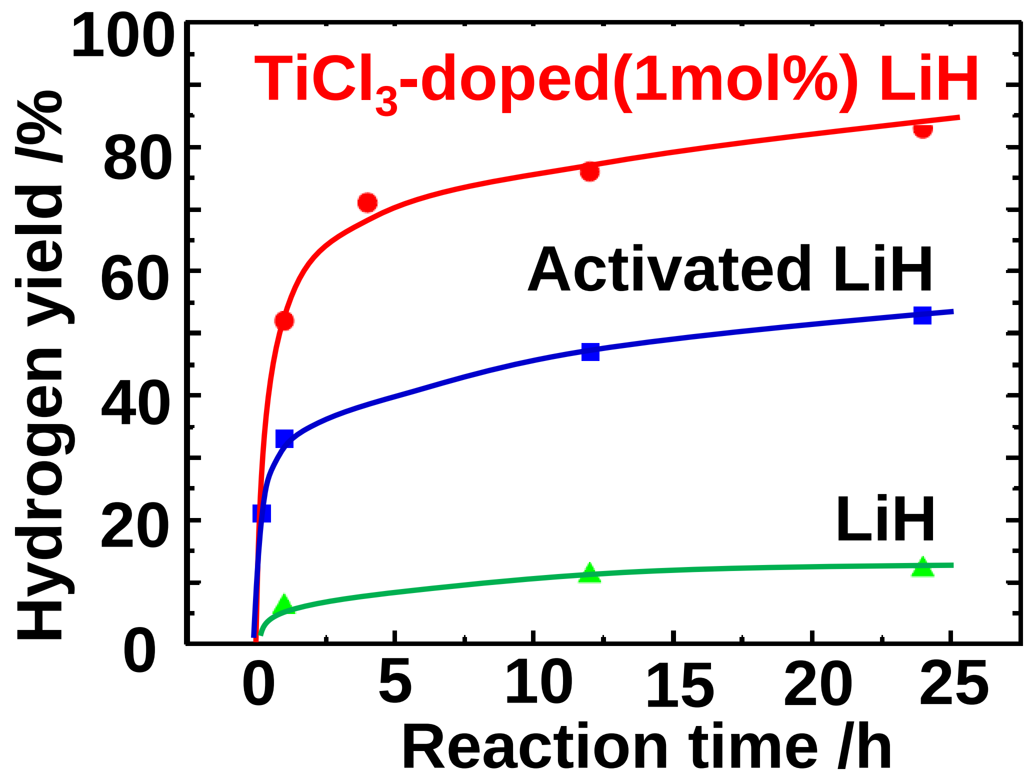
Y. Kojima, K. Tange, S. Hino, S. Isobe, M. Tsubota, K. Nakamura, M. Nakatake, H. Miyaoka, H. Yamamoto and T. Ichikawa, J. Mater. Res., 24, 2185 (2009)

Molecular dynamics simulation



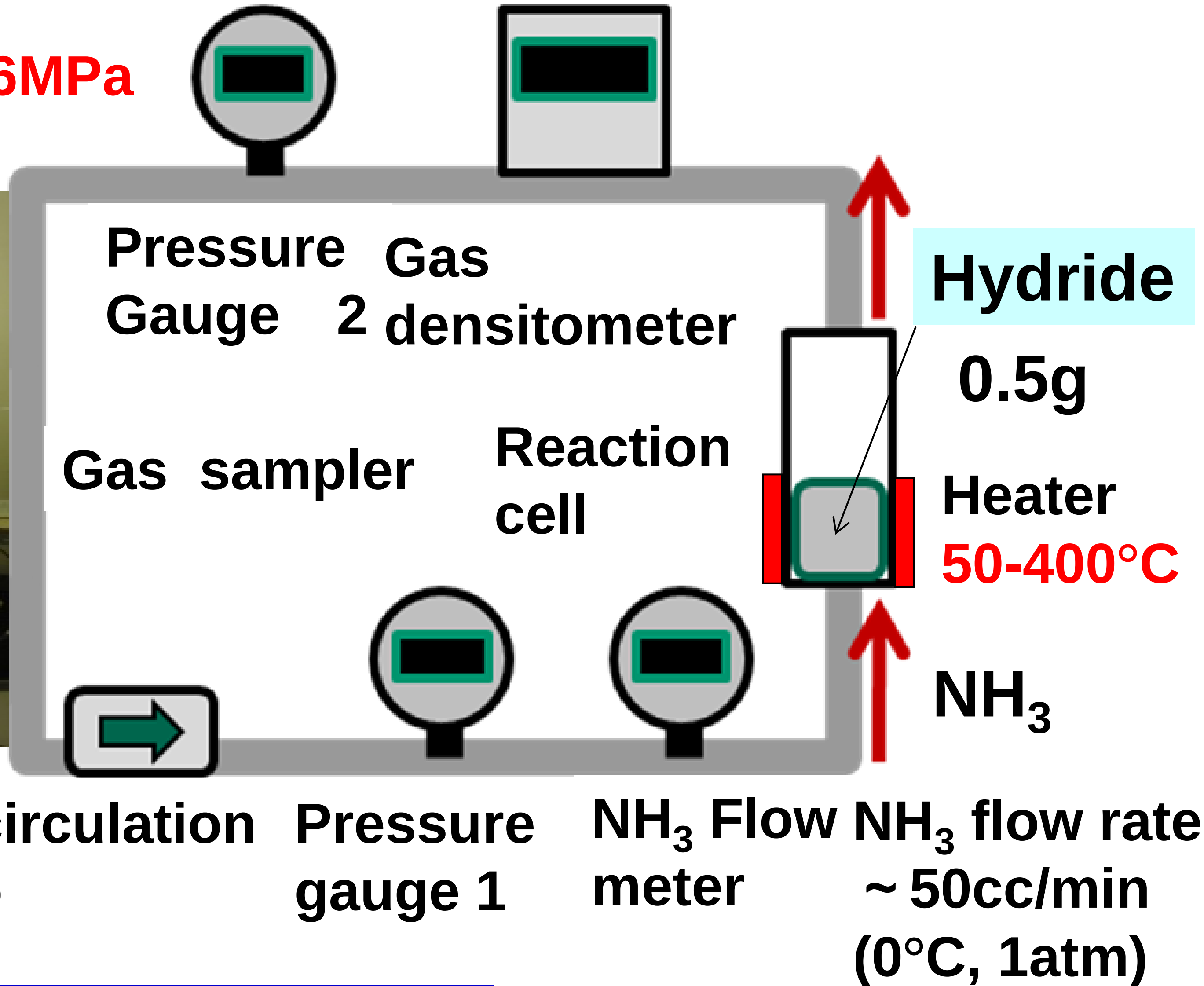
A. Yamane, F. Shimojo, K. Hoshino, T. Ichikawa, Y. Kojima J. Mol. Struct. THEOCHEM 944, 137 (9pp) (2010)

Hydrogen desorption curves of LiH-NH_3 system(room temperature)



Conversion system between NH_3 and H_2

$$NH_3 + LiH \leftrightarrow LiNH_2 + H_2$$

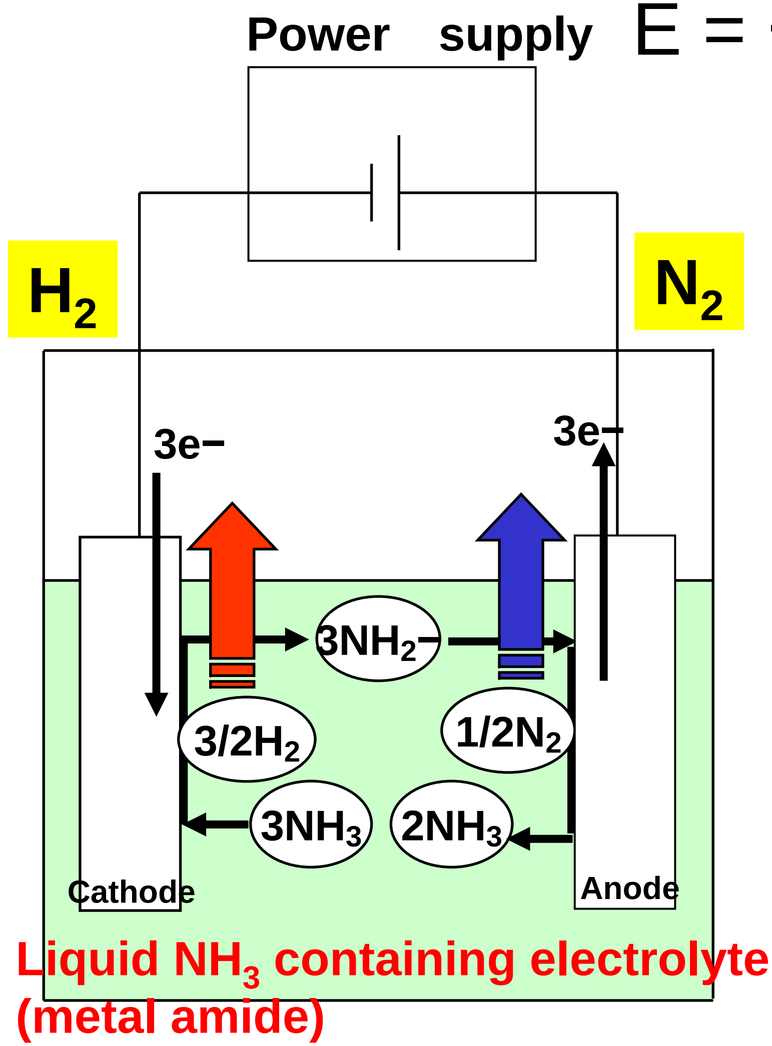


Collaborative research with Toyota Industries

Electrolysis of NH_3

$E(H_2O)=1.23V \rightarrow E(NH_3)$？

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



ΔG^0: Standard Gibbs free energy difference=13.1kJ/mol

n=3: Electron number responsible for reaction

E : Theoretical decomposition voltage

Vapor Pressure of NH_3 (25 ºC)

$$NH_3 \rightarrow 1/2N_2 + 3/2H_2$$

$E(NH_3)$=0.038V+ 0.039V=0.077V(theory)

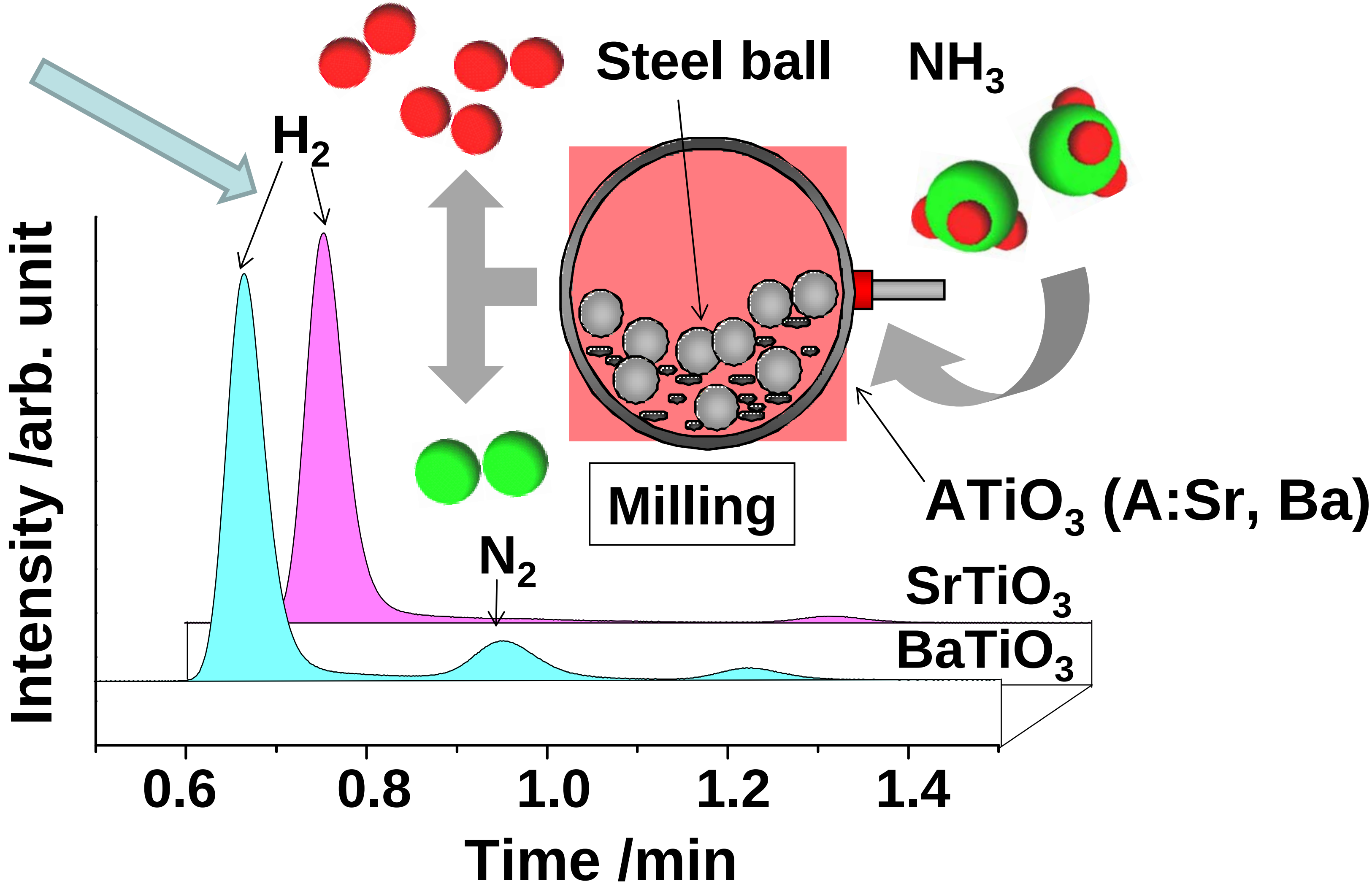
Cathode	Anode
$3NH_3 + 3e^- \rightarrow 3/2H_2 + 3NH_2^-$	$3NH_2^- \rightarrow 1/2N_2 + 2NH_3 + 3e^-$

0.5V(experimental)

N. Hanada, S. Hino, T. Ichikawa, H. Suzuki, K. Takai, Y. Kojima, Chemical Communications, 46, 3982-3984 (2010)

Mechanocatalysis

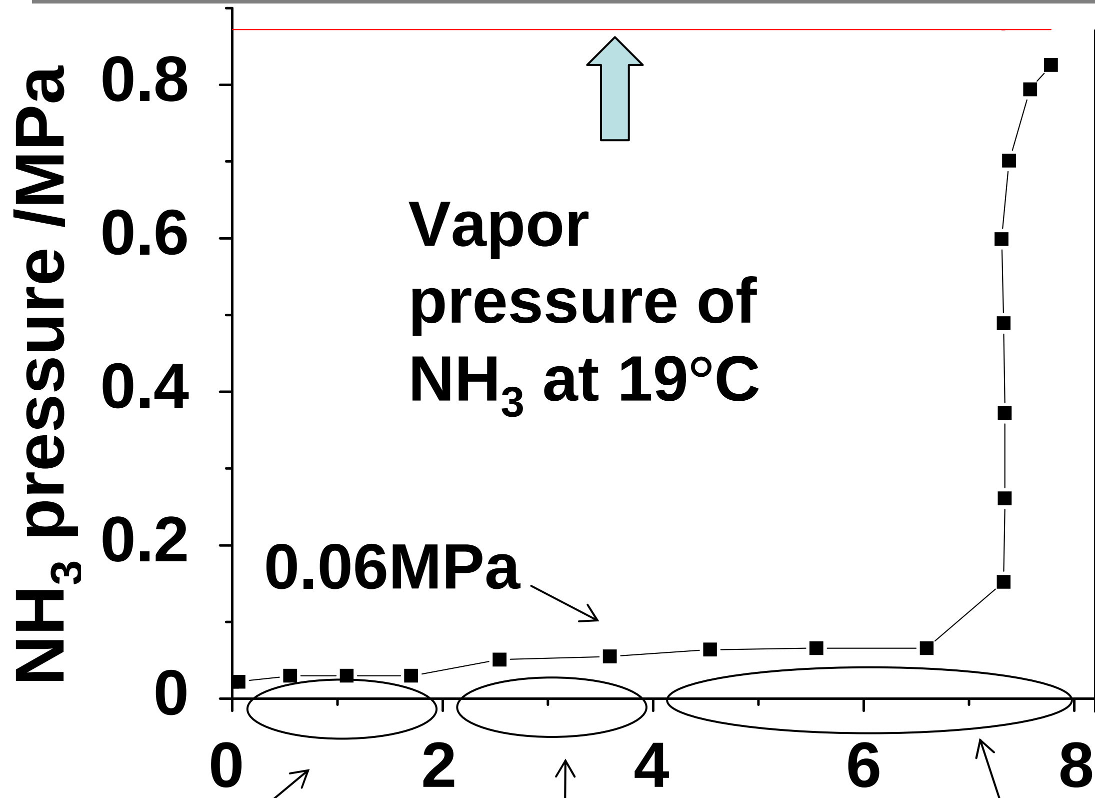
We have detected hydrogen and nitrogen gas when $SrTiO_3$ and $BaTiO_3$ powder is mechanically milled under ammonia gas at room temperature.



B. Paik, M. Tsubota, T. Ichikawa, Y. Kojima, Chemical Communications, 46, 3982-3984 (2010)

(2) NH_3 absorbing materials

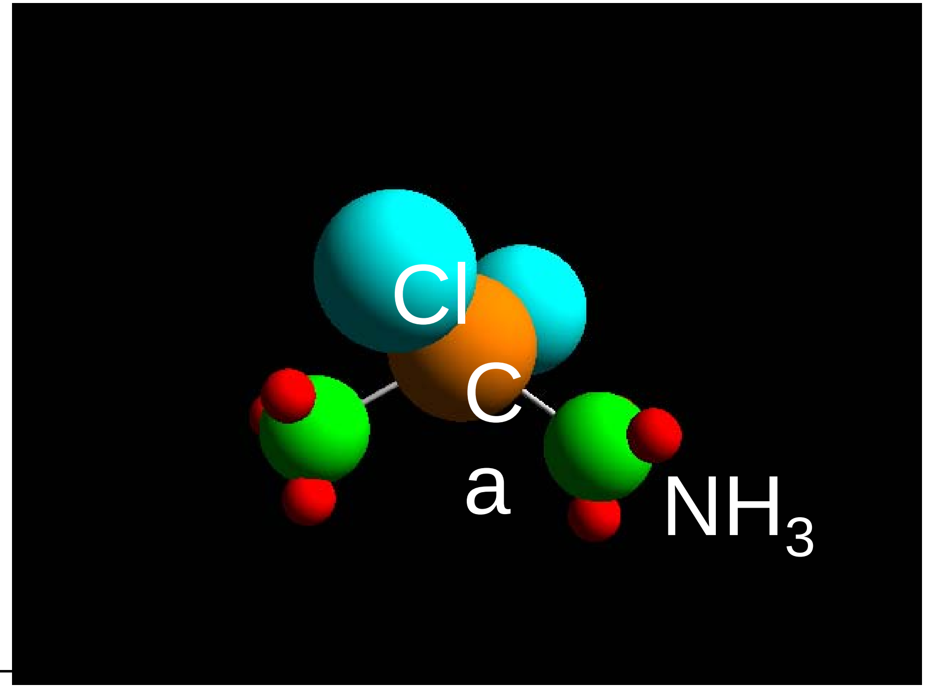
P-C isotherm for $CaCl_2$-NH_3 system



69-63kJ/mol

42kJ/mol

41kJ/mol



115g/L 107g/L

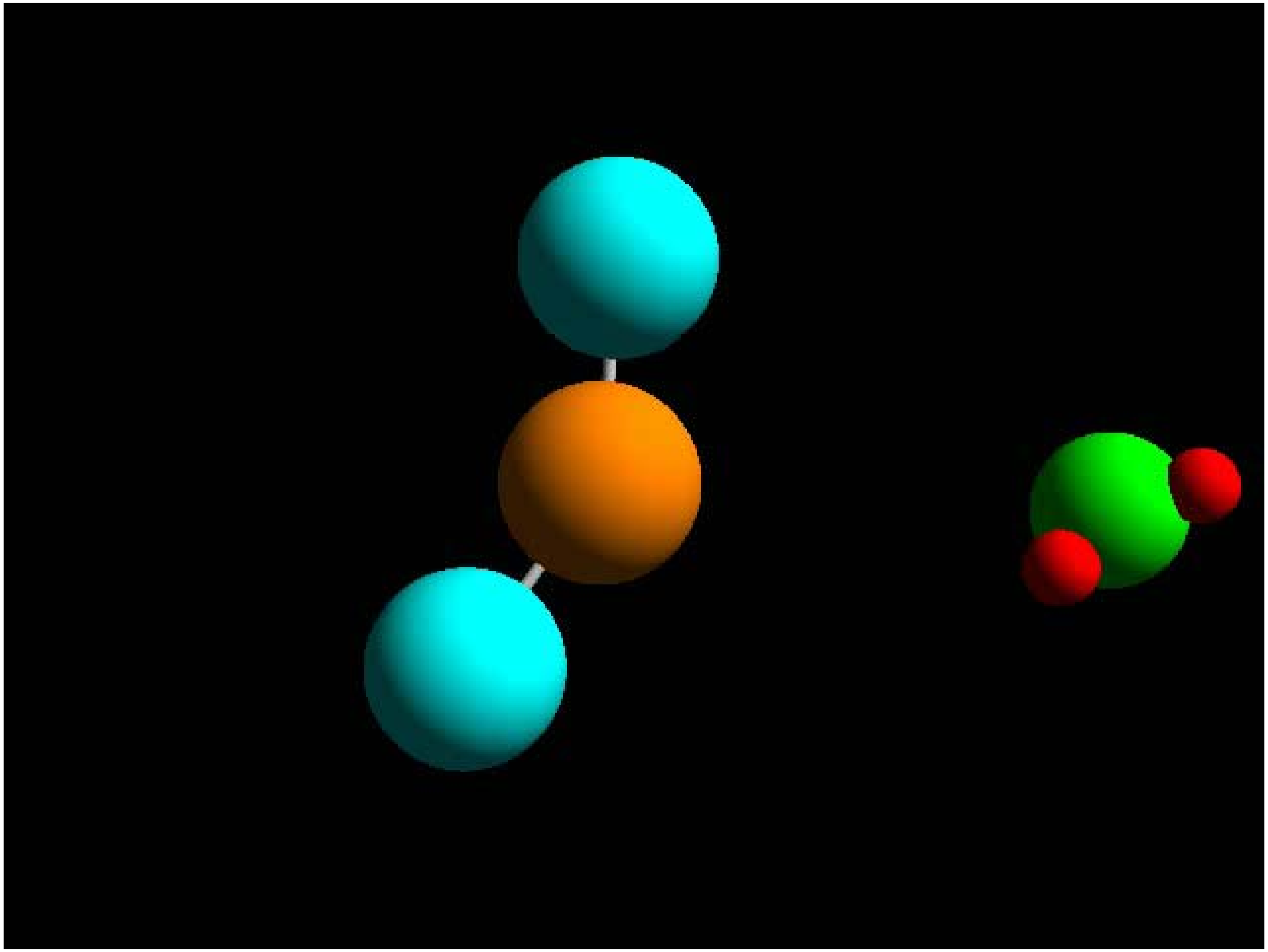
102kg $Ca(NH_3)_8Cl_2$

56kg Liquid NH_3

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

Rasmus Z. Sørensen et al., J. AM. CHEM. SOC. 130, 8660 (2008)

ab initio molecular-dynamics (MD) simulation based on density functional theory (DFT) .

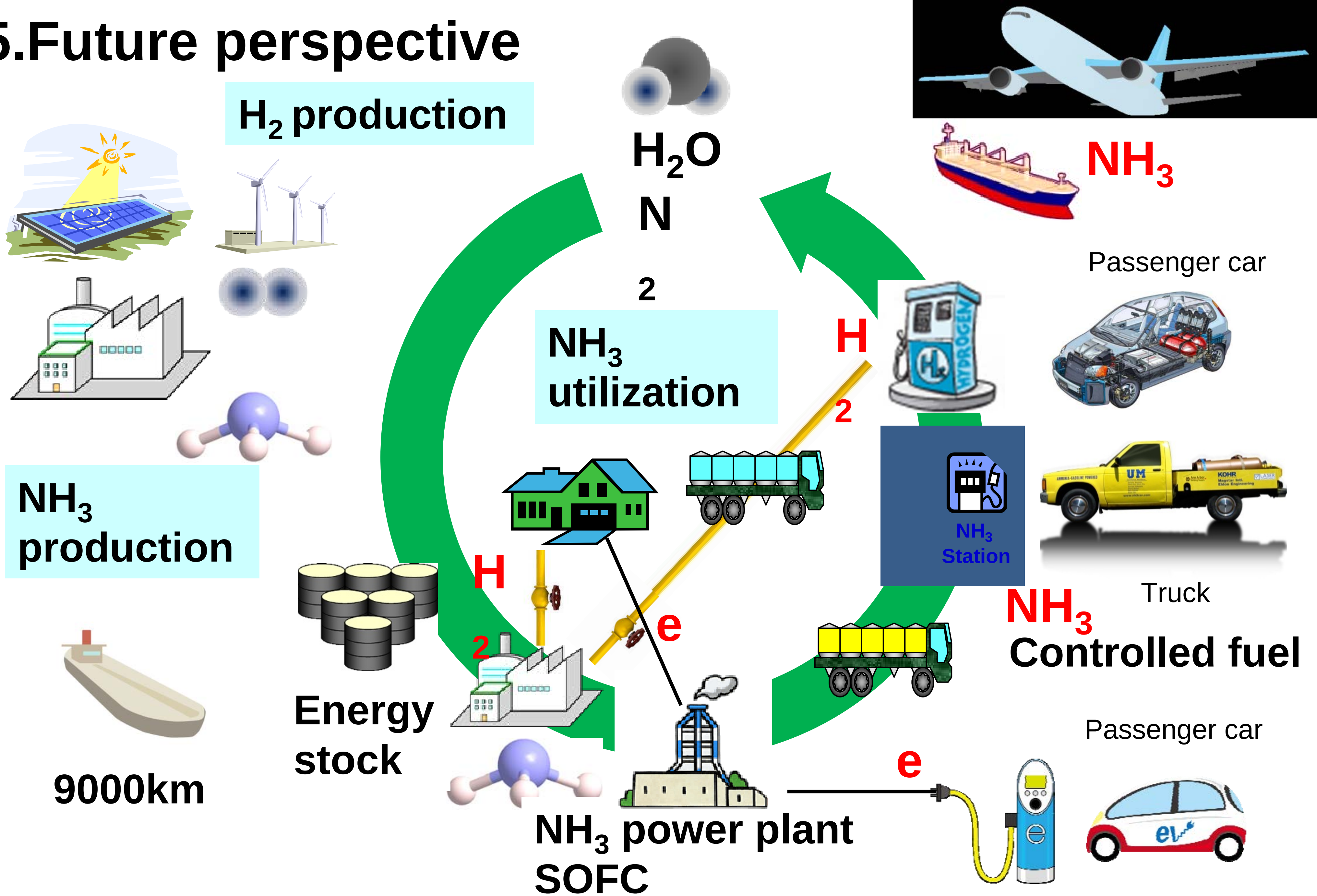


Lower vapor pressure

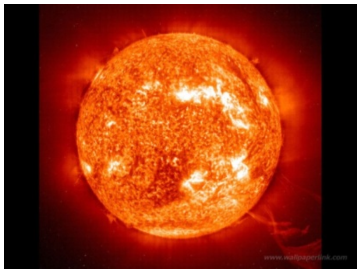
A. Yamane et ai., Abstract of MH2012, Kyoto Japan (2012)

Absorption energy

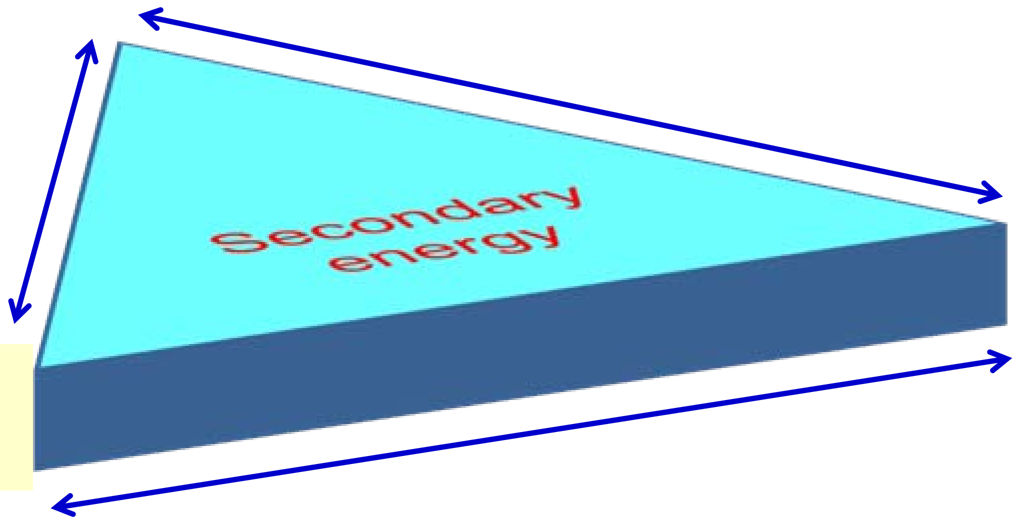
5.Future perspective



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



NH_3 Controlled fuel



H_2

Electricity

Best mix of NH_3, H_2 and electricity

6.Summary

HIROSHIMA UNIVERSITY IAMR

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

IAMR

経済新聞（夕刊）　2012年（平成24年）9月21日（金曜日）　©日本経済新聞社2012　（日刊）

日本経済新聞

夕刊

9月21日

（金曜日）

発行所　日本経済新聞社
東京本社　㈹(03)3270-0251
〒100-8066 東京都千代田区大手町1-3-7
大阪本社　㈹(06)6943-7111
名古屋支社　㈹(052)243-3311
西部支社　㈹(092)473-3300
電子版アドレス
http://www.nikkei.com/
購読のお申し込み
0120-21-4946
http://www.nikkei4946.com

水素燃料 輸送しやすく

液化技術の開発支援

政府、20年代実用化

政府はクリーンエネルギーの切り札とされる水素燃料の実用化に向けた技術開発に乗り出す。水素は気体で扱いにくいが、簡単に大量の水素を液化して輸送・貯蔵できる技術を確立し、普及を促す。2013年度から大学や石油会社と連携して研究に着手し、20年代の実用化をめざす。

水を電気で分解してつくる水素は燃やしても二酸化炭素（CO_2）を発生させず、環境負荷の小さい究極のクリーンエネルギーといわれる。だが、常温で気体なので持ち運びにくいほか、爆発の危険もある。

気体の水素を液体に変えるには、セ氏マイナス約253度まで冷却する必要がある。大規模な冷却装置がないと液体の状態を保てず、保管や輸送のコストが膨らむという欠点があった。

水素を簡単に、安く液化できる基礎技術の確立を急ぐため、経済産業省や文部科学省は技術開発費用として13年度予算案に20億円程度を計上したい考えだ。水素をそのまま冷やして液化する方法のほか、別の物質と反応させて別種の液体燃料に変える手法も候補になるという。

水素を液体に変えれば、トラックや船などで運びやすくなる。たとえば、風力発電施設などでつくった電気をかけて水を電気分解し、水素を取り出す。さらに気体の水

▼水素の液化技術　常温では気体で存在する水素は、セ氏マイナス約253度まで冷却すると液体に変わる。新しく確立するのは、水素にほかの物質を結びつけ、より簡単に液化する燃料を精製する技術。たとえば水素と窒素を反応させるとアンモニアになる。アンモニアは少し圧力をかけるだけで液化するため、液化や輸送のコストが軽減できる。また、純粋な水素だけでは爆発の危険性が高い。他の物質と結合して別種の液体燃料になれば、安全性も高められるという。

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

Liquid Hydrogen Fuel for Hydrogen Delivery

$20 million

September 21, 2012

Acknowledgement:

This work was partially supported by the “Advanced Fundamental Research Project on Hydrogen Storage Materials” supported by NEDO (2007-2011FY), Japan.

HIROSHIMA UNIVERSITY IAMR

Staff: 6, PD: 2, M1: 4, M2: 4, D1: 1, D2: 1, D3: 3, D4: 1,D5: 1 (24) (2012)

Emerging Fuels(DOE) → **Alternative Fuels ?**

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

Thank you for your attention.