Overview of R & D on Hydrogen Storage Materials in Japan

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Content

Japanese scenarios for introduction of

- Fuel cell vehicles
- Residential fuel cell

Application of hydrogen storage materials to hybrid tank system

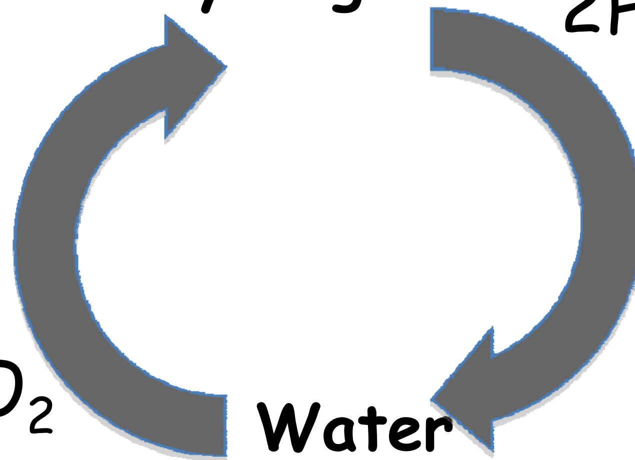
Fundamental research on hydrogen storage materials

Hydrogen/Water Cycle

Hydrogen

$2H_2 + O_2 \rightarrow 2H_2O$

Hydrogen Production



Work

$2H_2O \rightarrow 2H_2 + O_2$

Water

Global Cycle of **Hydrogen** compared to **Carbon**

The amount: Water is 27,000 times as much as Carbon

Transportation : Water is 3,160 times faster than Carbon

Because of **less impact to environment**, Hydrogen/Water cycle is superior to the carbon cycle as material circulation for energy system of mankind.

(Ken-ichiro Ota, WHEC 16, 13-16 June 2006, Lyon, France)

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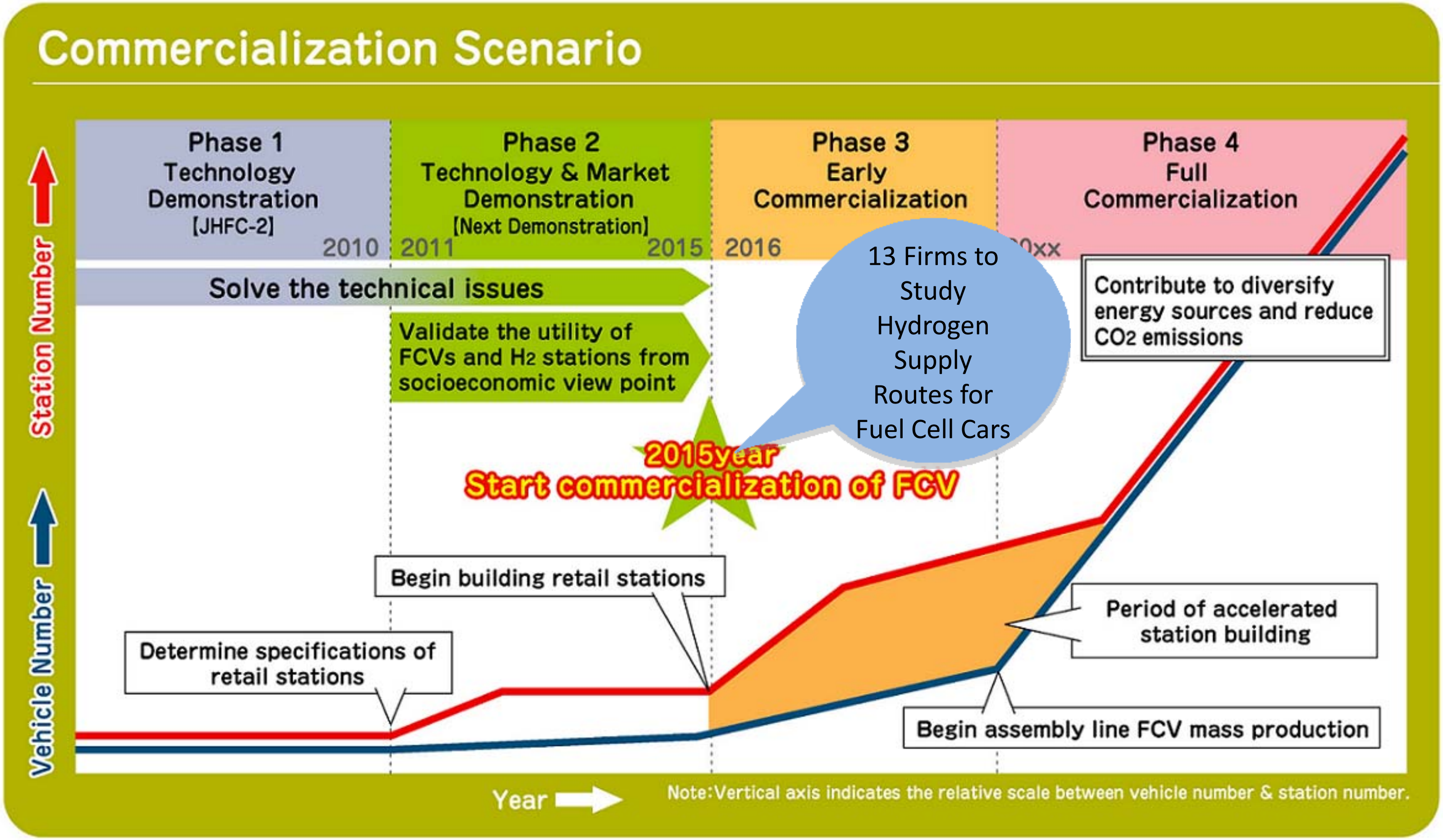
Fuel Cell Market Entry

Commercialization of FCV and hydrogen refueling stations

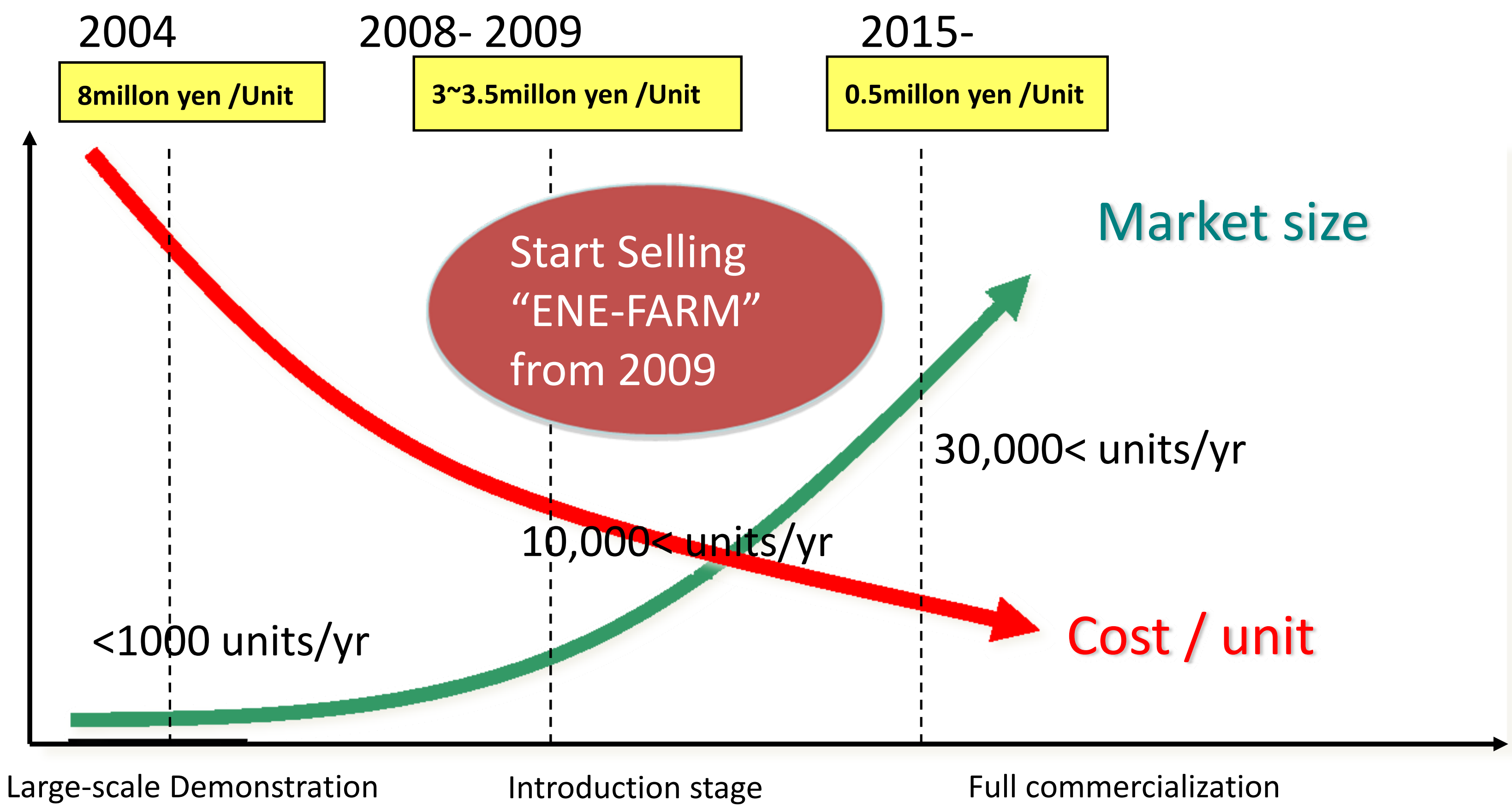


Leading automakers in and outside Japan and Japanese energy companies have agreed on a scenario which sees commercialization of fuel cell vehicles (FCVs) and hydrogen stations beginning in 2015.

AIST Source : FCCJ, http://www.fccj.jp/pdf/20080704sks1e.pdf

Scenario of Market Creation for Residential Fuel Cell

Large-scale Demonstration Project → Market creation by government support → Full commercialization Self sustained and growing market



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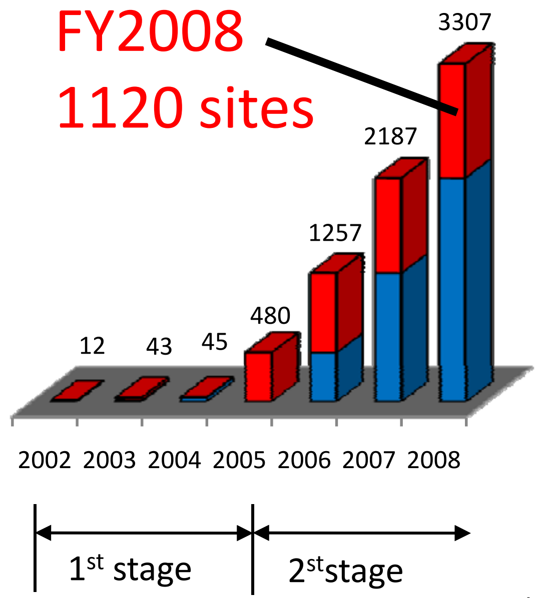
Large-Scale Stationary Fuel Cell Demonstration Project
- Experience of over 3,000 installations -

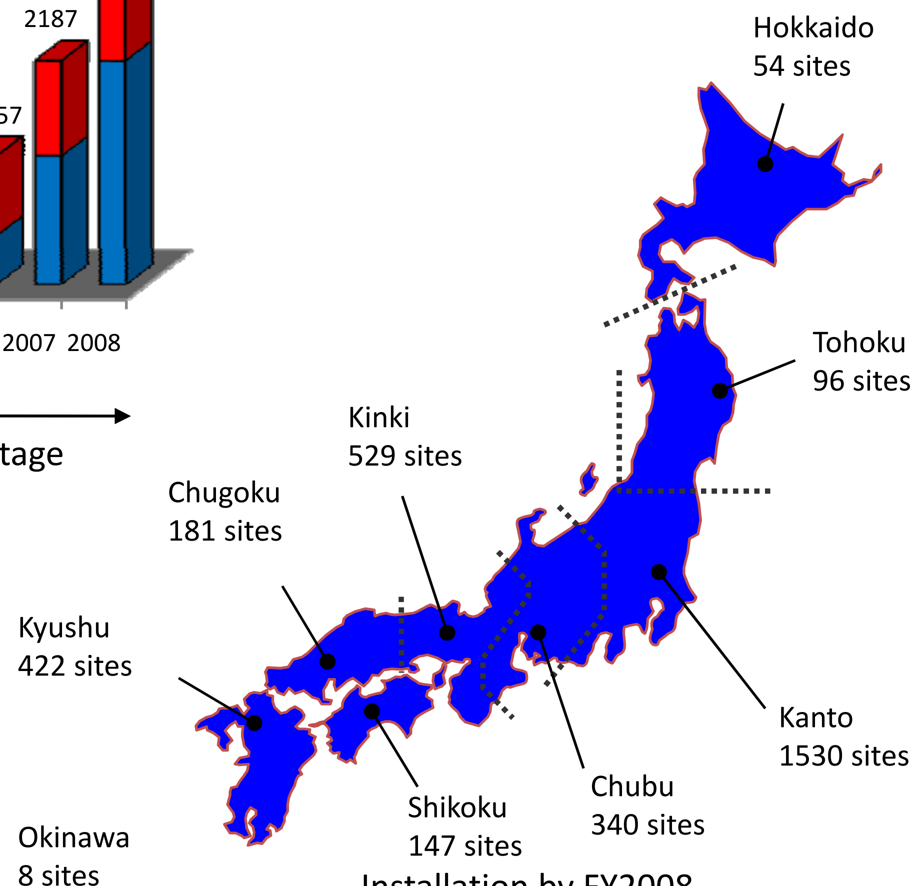
Reduction

Energy Consumption : 24%
CO2 Emissions : 39%

※Based on data from 83 homes where top performing systems were installed in FY2006

Residential FC 1 kW class





Installation by FY2008

Breakdown by Fuel

Fuel	Systems
LPG(Propane)	1,614
Natural Gas	1,379
Kerosene	314
Total	3,307

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Fuel Cell Market Entry
- Commercialization of Residential Fuel Cells -

"ENE-FARM" is the common name of the products

"The first shipping" ceremony of residential fuel cell systems at ENEOS company on July 1, 2009

Production capacity : 10,000 units/year
40,000 units/year by 2015

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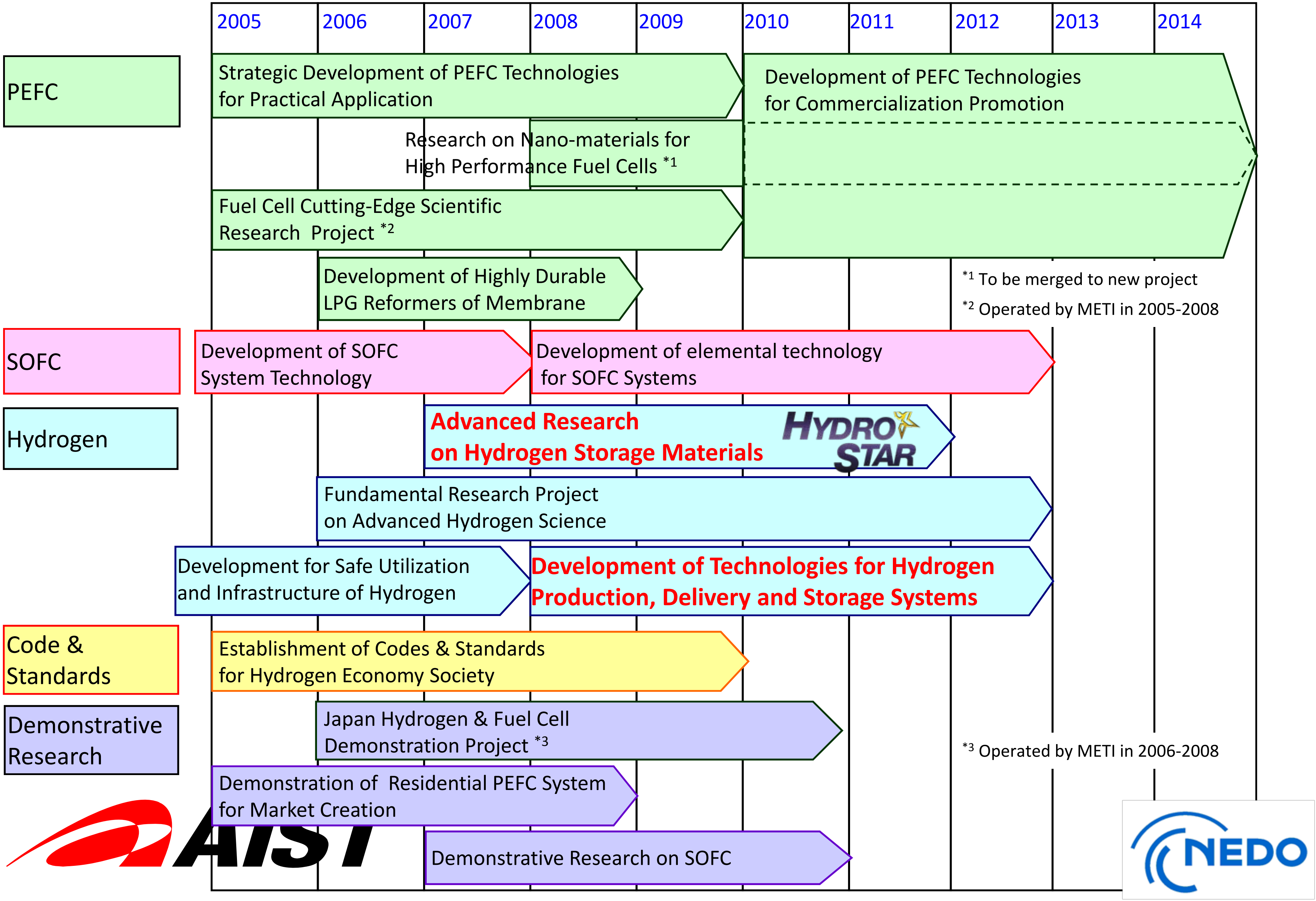
R&D on Fuel Cell and Hydrogen Technologies at NEDO



Back to Basic Policy

For further development, fundamental research is indispensable

From FY 2005 Japanese government initiated fundamental research projects for fuel cell and hydrogen

- Fuel Cell Cutting-Edge Scientific Research Project (FC cubic) : FY2005-2009
- Fundamental Research Project on Advanced Hydrogen Science (HYDROGENIOUS): FY2006-2012
- Advanced fundamental research for hydrogen storage materials (HYDRO☆STAR): FY2007-2011
- Research on Nano-materials for High Performance Fuel Cells (HiPer-FC) : FY2008-2014

Advanced Fundamental Research Project on Hydrogen Storage Materials

Term：FY2007～FY2011　Budget FY07： 740MYen, FY08: 908MYen, FY09 1,000MYen

To establish compact and energy efficient hydrogen storage system through fundamental studies of materials

Background

○ To realize compact and energy efficient hydrogen storage is a key technology

○ Japanese technology of hydrogen storage materials is significantly competitive

○ Breakthroughs in hydrogen densities are strongly required

Plan

○ Make network among research labs

○ Invite young scientists from other fields

○ Large scale facilities such as Spring-8 (synchrotron X-ray) and J-PARC (Neutron) should be used for characterization

○ Combine experiments and computation

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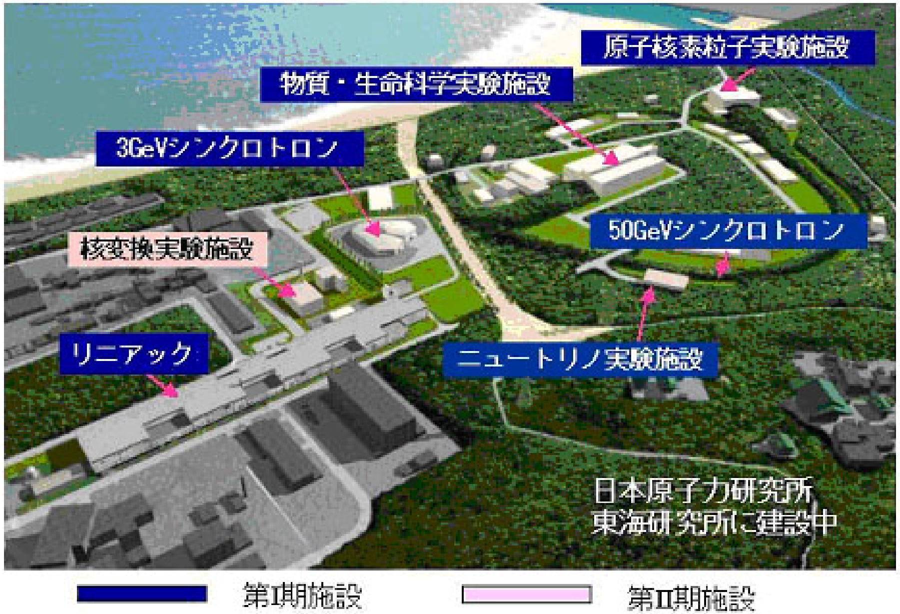
HYDRO STAR

Synchrotron radiation and Pulsed neutron SPring-8 & J-PARC



J-PARC

Spallation neutron source
Operated from 2008

Total scattering spectrometer "NOVA" for in-situ measurements under H_2 has been constructed

SPring-8

The 3rd Generation Synchrotron radiation source

Hydrogen-Metal interaction under high-pressure has been studied

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Total neutron scattering

- Hydrogen can not be detected using X-ray.
- Neutron is only a tool for hydrogen research especially for structure analysis.

- Total scattering = Bragg diffraction + diffuse scattering

- Pair distribution function (PDF) can be calculated from total scattering data. It includes correlation (distance and coordination number) of two elements in any form of materials such as crystalline, nano particles, amorphous and liquid.

NOVA: Total scattering spectrometer for hydride research at BL21, J-PARC

Hydrogen Storage Materials

Interstitial Hydrides

（Hydrogen Absorbing Alloys)

Non-interstitial Hydrides

- Saline Hydrides

- Complex Hydrides (Covalent Hydrides)

- Organic Hydrides

- Adsorbents

- Clathrates

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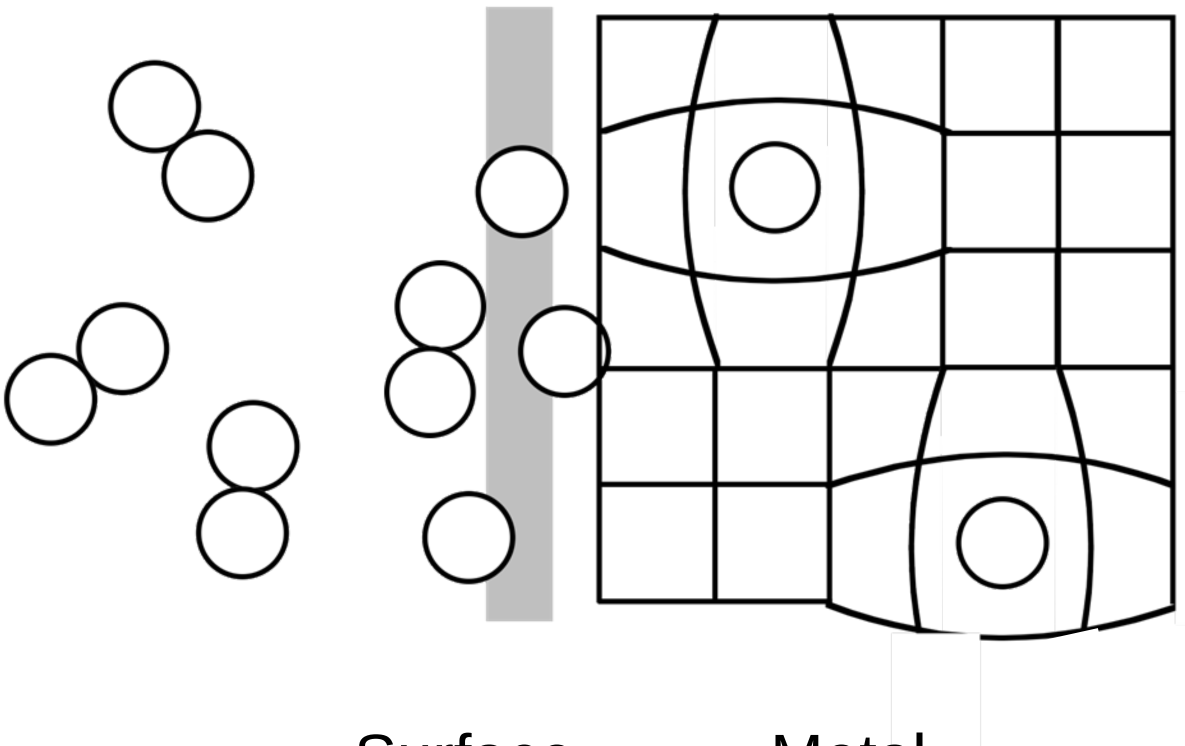
Interstitial Hydrides



Hydrogen molecule (H_2) Surface Metal lattice

Ni-Hydrogen Battery

discharge

Cathode $NiOOH + H_2O + e^- \Leftrightarrow Ni(OH)_2 + OH^-$

charge

Anode $MH + OH^- \Leftrightarrow M + H_2O + e^-$

Hydrogenated alloy (MH) | Dehydrogenated alloy (M)

Overall $NiOOH + MH \Leftrightarrow Ni(OH)_2 + M$

Ni-Hydrogen Battery
Environmental Friendly

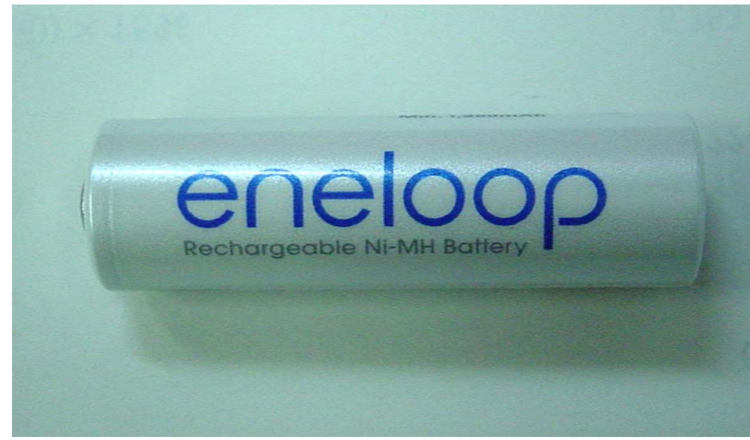
Minimized self-discharge

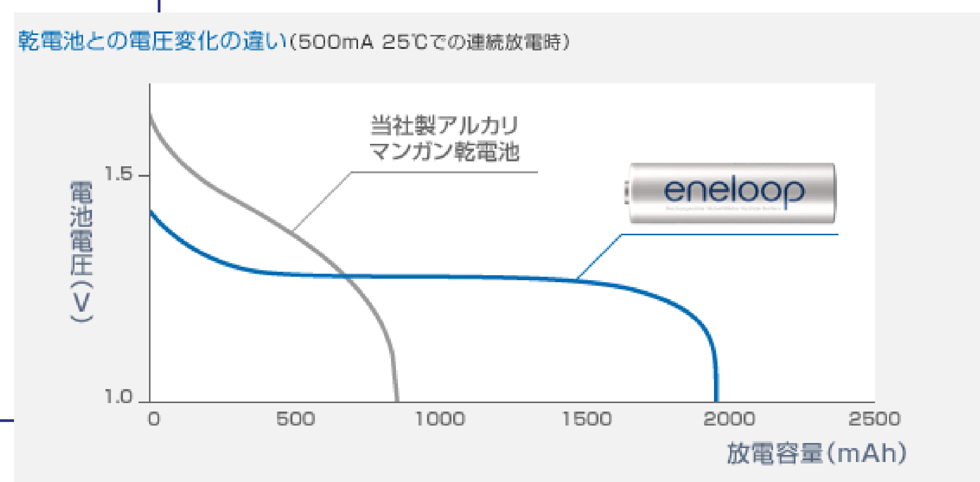
- One year after charging
  - eneloop 85 % remained
  - Others 0 %

Can be used as dry battery

New material (Superlattice Alloy) was developed

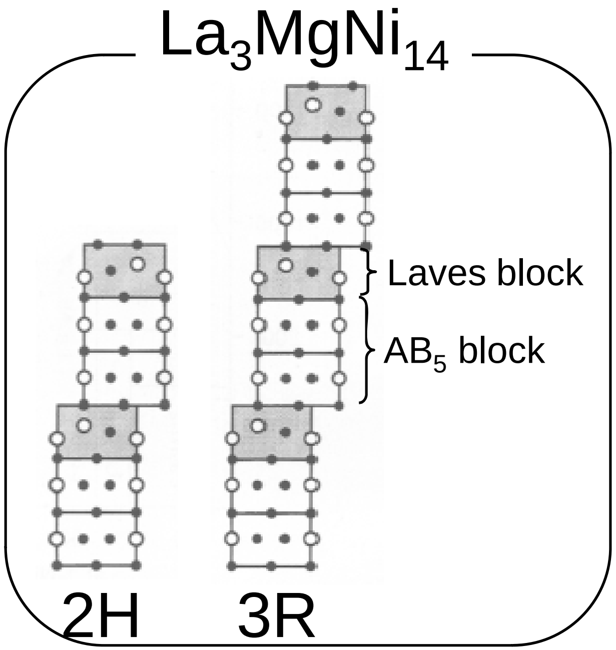
Awarded many times

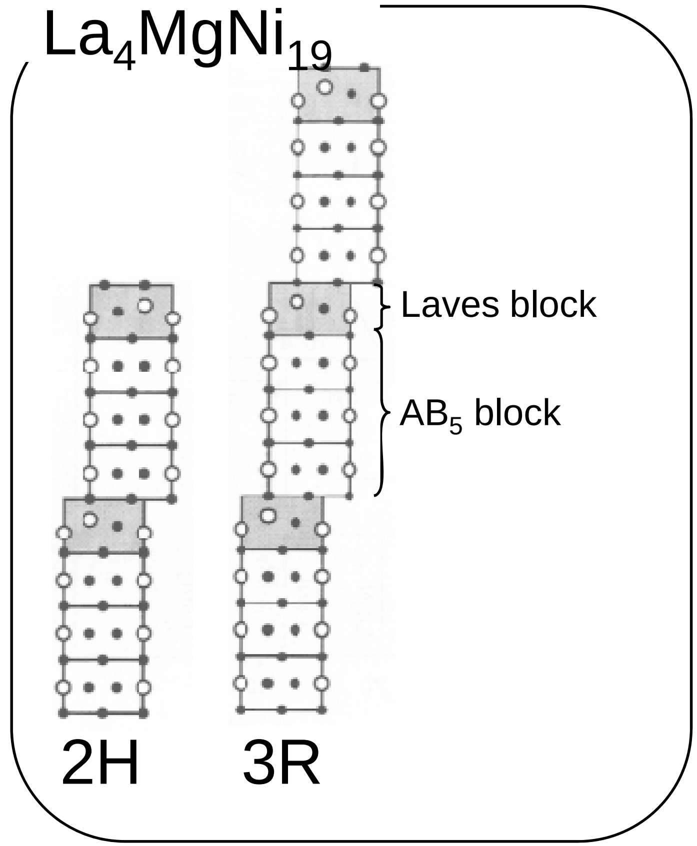




http://www.sanyo.co.jp/eneloop/info/info11.html

Superlattice alloy





Y. Komura, Phase Transitions
16/17 (1989) 495-507

T. Yamamoto *et al.*, Acta Mater.
45 (1997) 5213-5221

H. Hayakawa *et al.*, Mat. Trans.
46 (2005) 1393-1401

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Hydrogen Storage on board is a Key

State-of-art of FCV: over 100 km cruising by 1 kg of hydrogen

Target of Volume density

5 kg of hydrogen in 100 L tank（>50g/L）

Target of Weight density

5 kg of hydrogen in 100 kg tank（>5 mass %）

There is no realistic solution for on board hydrogen storage

	Volume density	Weight density
Compressed gas (35MPa)	25g/L	~5 %
Liquid hydrogen	60g/L	~5 %
Hydrogen storage materials	50g/L	~2 %

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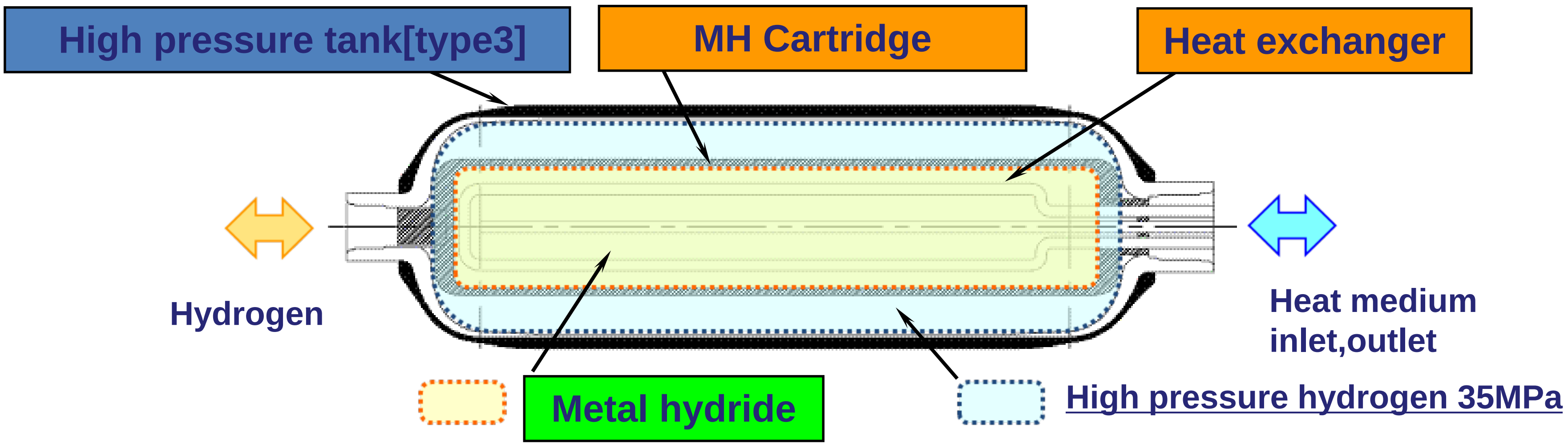
Hybrid tank system

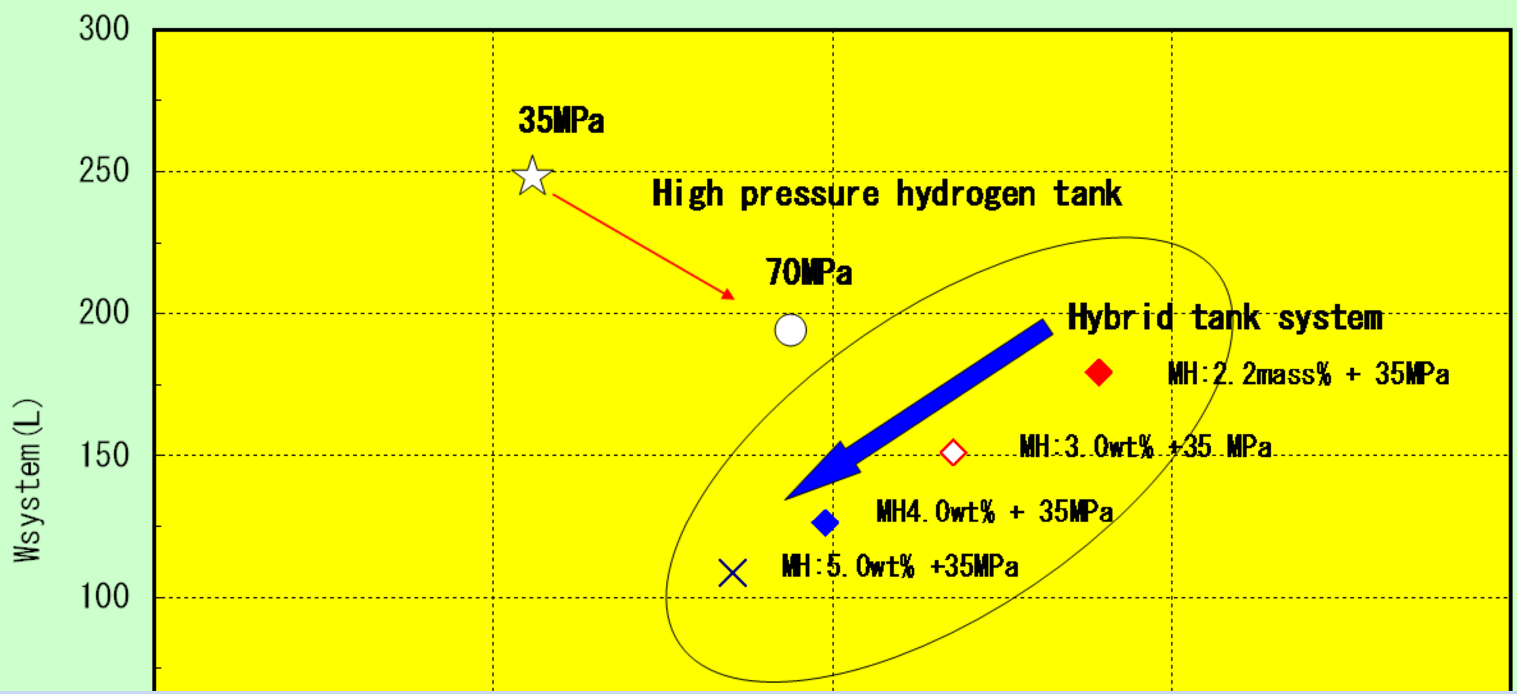


NEDO

Development of Technologies for Hydrogen Production, Delivery and Storage Systems

- High pressure tank[type3] : Samtech
- MH Cartridge , Heat exchanger : JMC , Saga University
- Metal hydride: AIST , JMC

Hydrogen Storage Technology



Hybrid tank: combination of high pressure and hydrogen storage materials

Hybrid tank provides higher volume density than compressed hydrogen

Hydrogen 5[kg] system weight[kg] and volume[L]

Non-interstitial Hydrides

Saline Hydrides

NaH, MgH_2, AlH_3 （cf. NaF, MgF_2, AlF_3)

Complex Hydrides (Covalent Hydrides)

$NaAlH_4$, $LiNH_2$, $LiBH_4$

Organic Hydrides

Adsorbents

Carbon, Zeolite, MOF

Clathrates

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Alane: AlH_3

Metal hydride with hydrogen capacity of 10.1 wt.%, 148 kg/m^3

Decomposition temperate is between 100° C and 200° C

Direct synthesis has not been reported

$$AlH_3 \rightarrow Al + 3/2H_2$$

Extremely high potential for on board application

High temperature and high pressure reactions and in-situ synchrotron X-ray diffraction

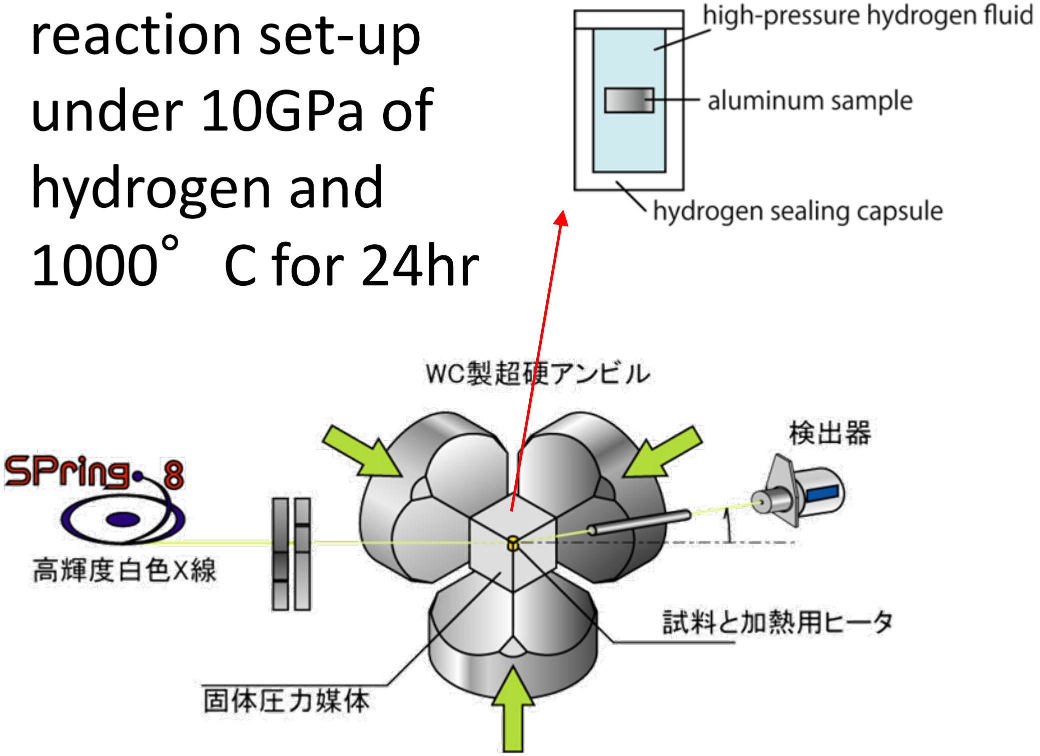
HYDRO STAR

Al foil（Nilaco, purity 6N）

Thickness of surface layers：35 Å (using XPS)

High temperature, high pressure X-ray diffractometer(BL14B1@SPring-8）

Development of reaction set-up under 10GPa of hydrogen and 1000° C for 24hr



H. Saitoh *et al*, *A.P.L.* **93**, 151918 (2008).
H. Saitoh *et al*, *A.P.L.* **94**, 151915 (2009).

Results will be shown by Dr. Saito of JAEA@SPring-8

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LiH and Ammonia System

Exothermic hydrogen desorption

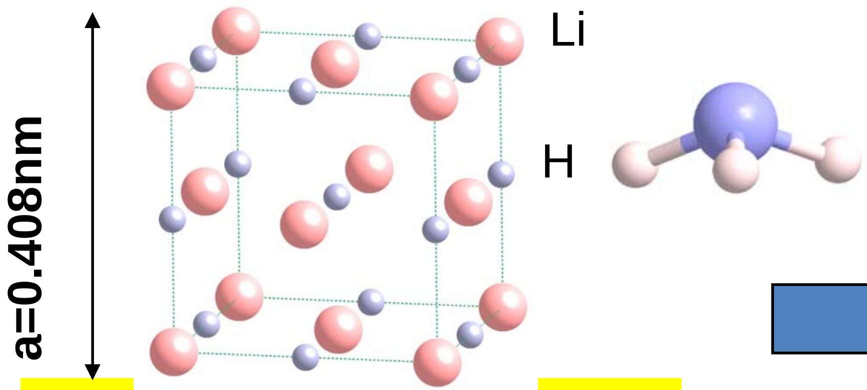
523K-573K

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

Desorption at RT

ΔH_0: -43kJ/molH$_2$ Capacity:8.1mass%

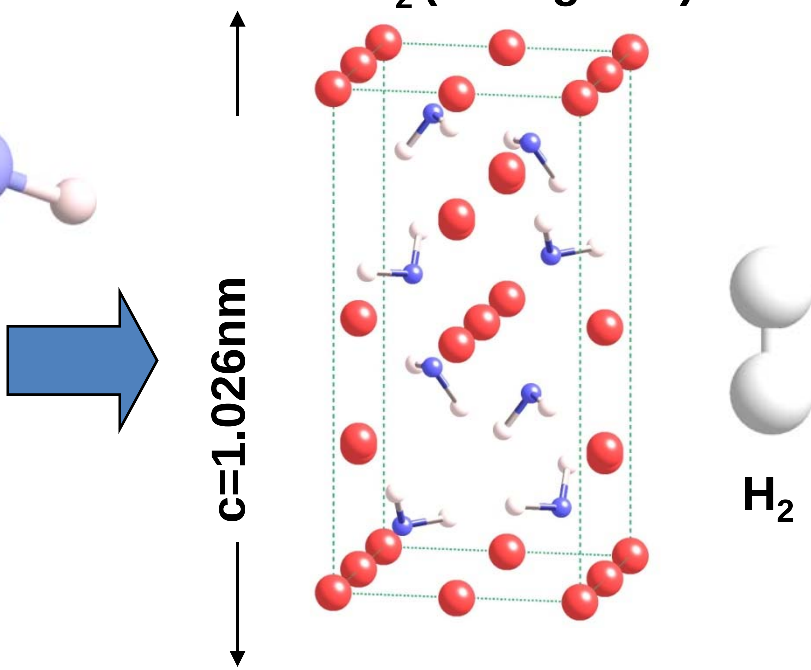
LiH(Cubic)



LiH: activated by milling

H2 release: 5mass%(Expt)

$LiNH_2$ (Tetragonal)



Zeolite Templated Carbon (ZTC)

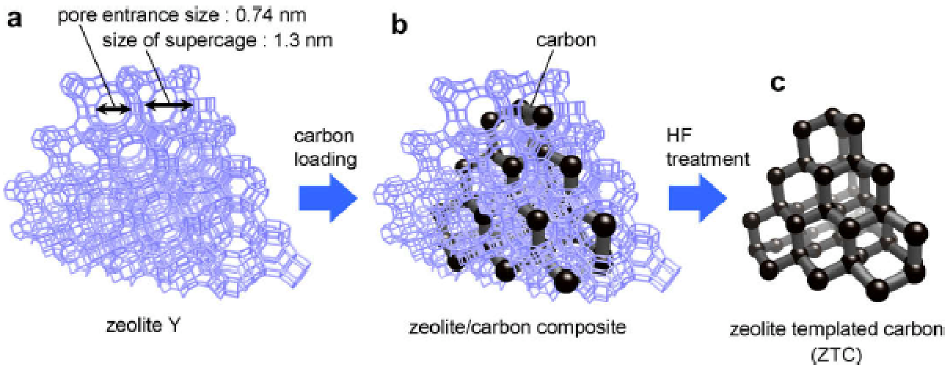
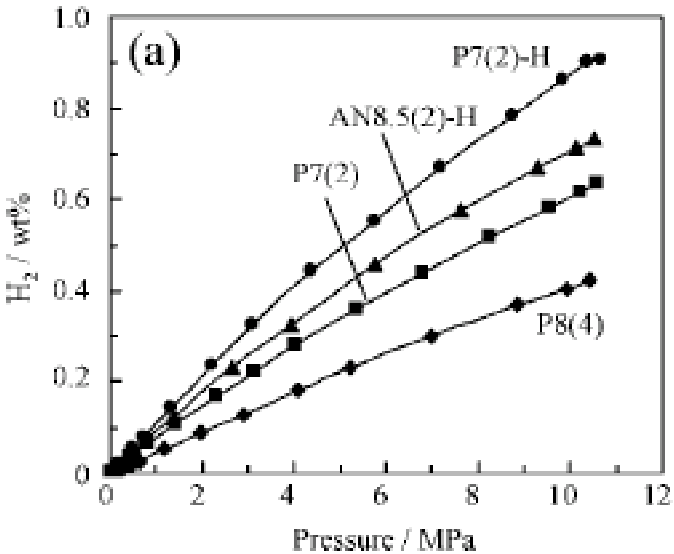


Fig. 1 – Synthesis procedure of the zeolite templated carbon (ZTC). (a) Crystal structure of the zeolite Y template, (b) illustration of zeolite/carbon composite. Impregnated carbon is shown by a black framework and (c) framework structure of the liberated ZTC after HF washing.

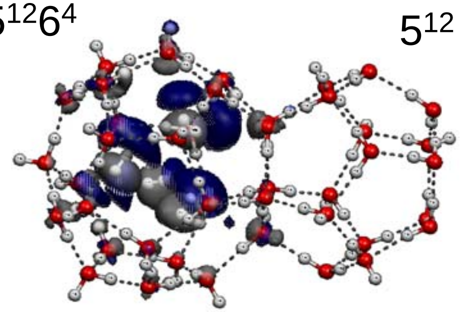
H. Nishihara et al., *J. Phys Chem. C*, **2009**, 113, 3189.



H. Nishihara et al., *Carbon*, **47**, 1220 (2009).

Computational Approach to Develop Novel Materials

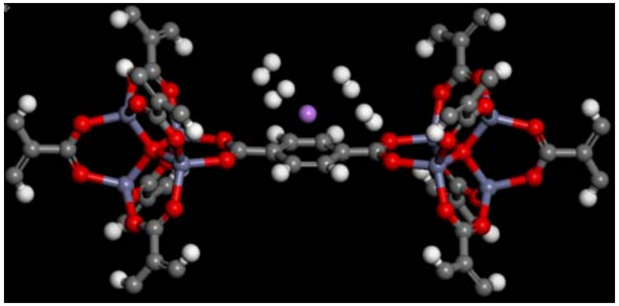
Clathrate hydorate



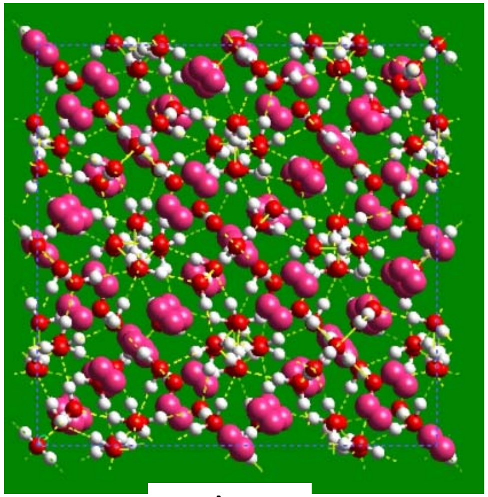
Cages in Clathrate molecule

Hydrogen molecule stored in micro space in molecules

MOF



LiMOF-5 – $4H_2$

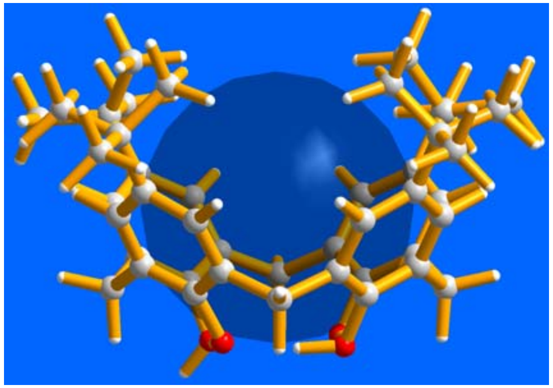


Hydrate

DFT calculations

- **H capacity**
- **Thermodynamic properties**
- **Hydrogen pressure**

TOMBO, VASP, Gaussian



Micro pore organometallic materials

Summary

•Japan has clear scenarios for introduction of fuel cells and fuel cell vehicles.

•Hydrogen storage is key technology to realize the hydrogen economy.

•Fundamental research of the hydrogen storage materials are intensively carried out at present under "Advanced Fundamental Research Project on Hydrogen Storage Materials".

•Development of on board tank is also conducted by industry and under the national project "Development of Technologies for Hydrogen Production, Delivery and Storage Systems .

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