Recent Progress in Research and Development of Hydrogen Storage Materials in Japan
Fundamental Research to Practical Application

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Content

Japanese scenario for introduction of

- Fuel cell vehicles
- Residential fuel cell

Fundamental research on advanced materials

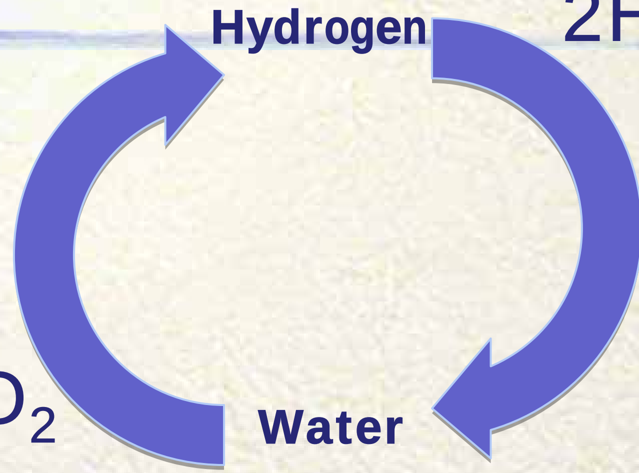
- Hydrogen storage materials

International Collaboration

Hydrogen/Water Cycle

$2H_2 + O_2 \rightarrow 2H_2O$

Hydrogen Production



Work

$2H_2O \rightarrow 2H_2 + O_2$

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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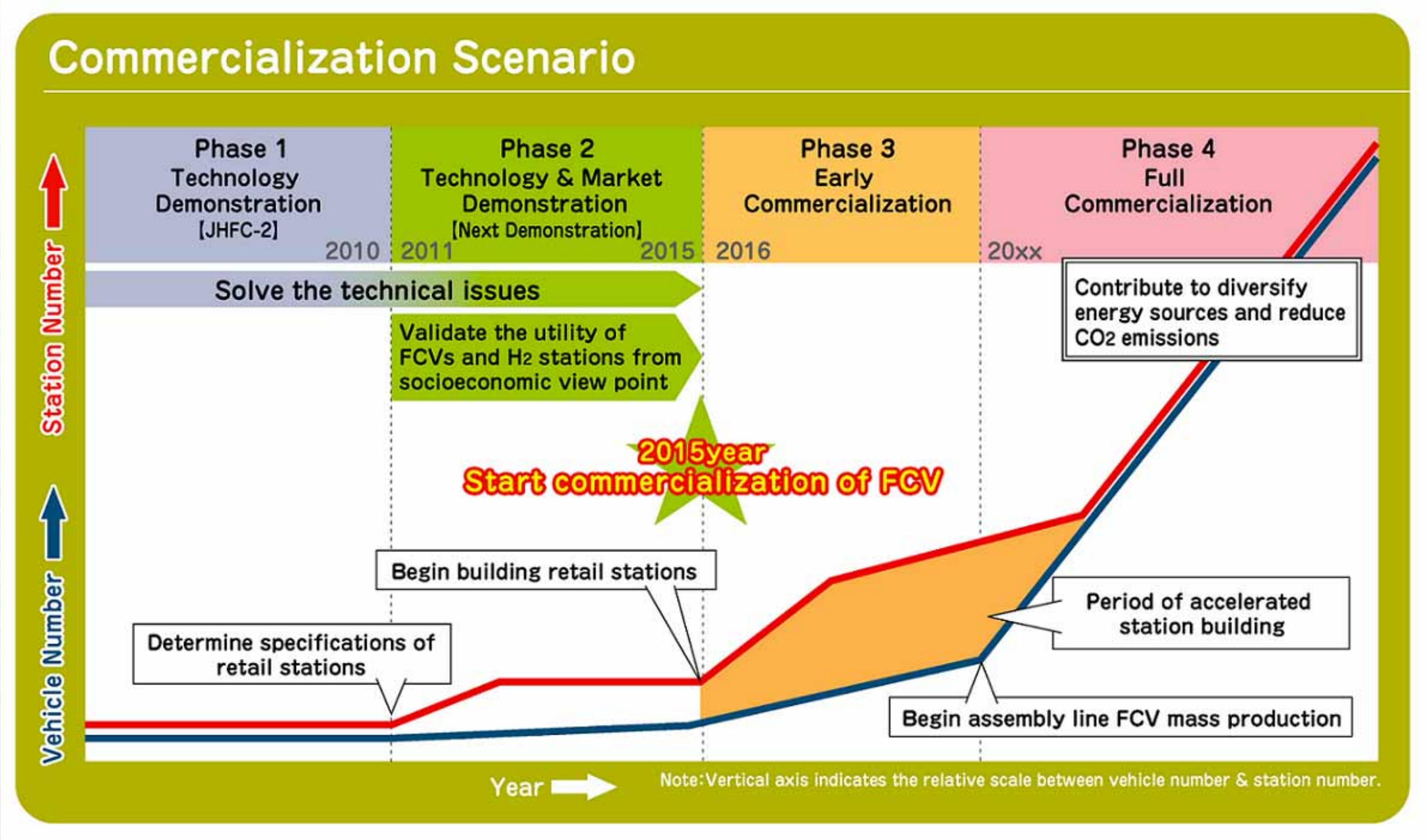
Fuel Cell Market Entry

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.

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

13 Firms to Study Hydrogen Supply Routes for Fuel Cell Cars

Tuesday, August 4, 2009

TOKYO (Nikkei)--**Nippon Oil Corp**., **Tokyo Gas Co**. and **11 other companies** said on Tuesday **that they will conduct joint research with an aim to commercialize technologies for supplying hydrogen to fuel cell vehicles by fiscal 2015.**

Other participants include **Idemitsu Kosan Co**., **Showa Shell Sekiyu KK**, **Osaka Gas Co**. and **Toho Gas Co**. Automakers are said to be considering joining the group.

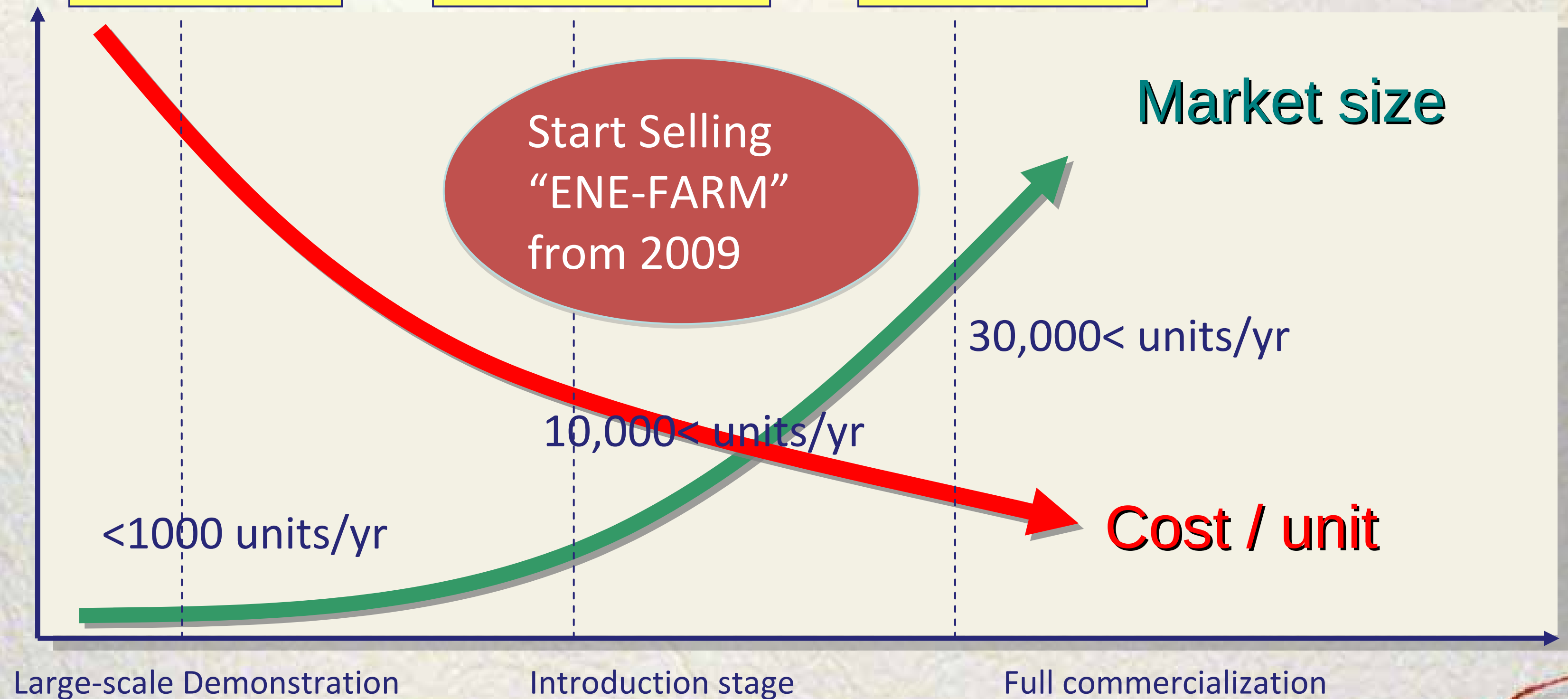
The research alliance will conduct field trials by setting up dozens of hydrogen stations across Japan. By using the oil companies' hydrogen production facilities and the pipelines of the gas companies, the group will research ways to transport the fuel to filling stations in a stable manner at low cost.

Some of the stations are to be built in urban areas and on highways, such as at existing gasoline-pumping depots. **The group hopes to eventually lower supply costs to levels comparable to gasoline**.

Scenario of Market Creation for Residential Fuel Cell

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

2004	2008- 2009	2015-
8millon yen /Unit	3~3.5millon yen /Unit	0.5millon yen /Unit



0.5 M JPY = 55,000 US$ = 375,000 RMB

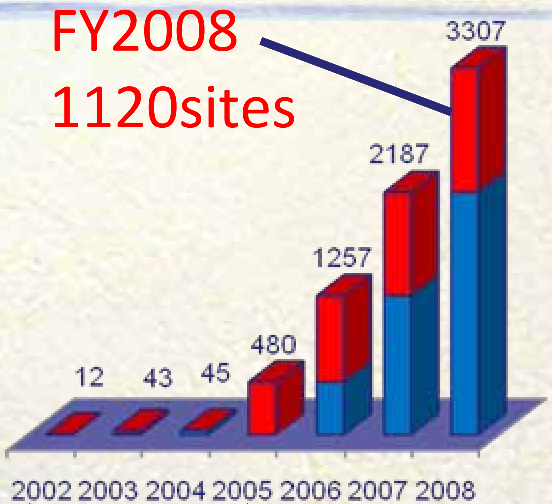
Large-Scale Stationary Fuel Cell Demonstration Project
- Experience of over 3,000 installations -

Residential FC 1 kW class

Reduction [**Energy Consumption : 24%**
CO_2Emissions : 39%]

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

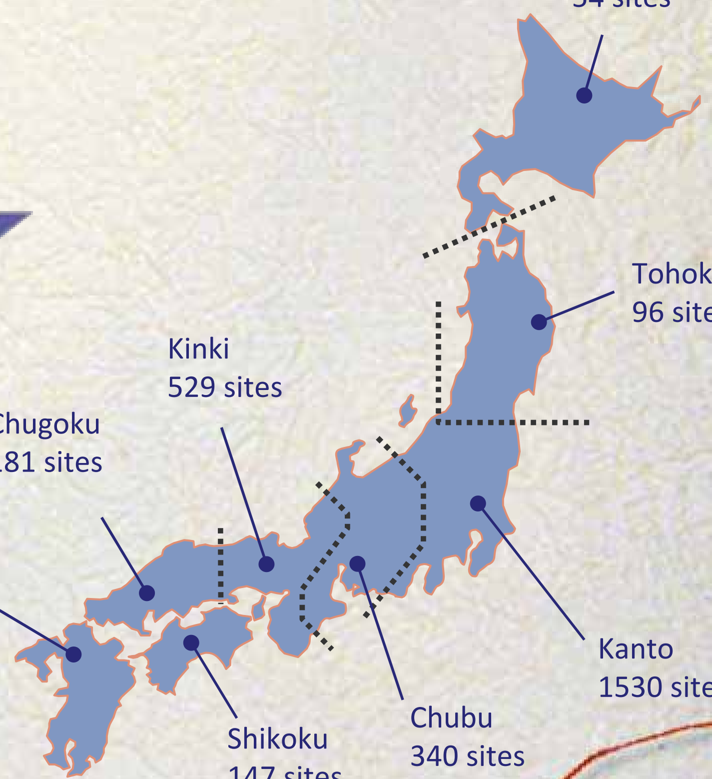
FY2008
1120sites



1st stage | 2nd stage

Breakdown by Fuel

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



Installation by FY2008

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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Expected Targets and Policies

FCV →  commercialization (2015)

Stationary FC →  20~100MW (2010)
2,500MW (2030)

	R&D Stage	Introduction Stage	Diffusion Stage	Full-Scale Diffusion Stage
Infra	Demonstration Project	Stepwise Construction	Market growth without support	Organic Growth
Codes	Review of Regulations			
R&D	R&D on FC and H_2	Further R&D for higher performance and low cost		

R&D on Fuel Cell and Hydrogen Technologies at NEDO

2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014

PEFC

Strategic Development of PEFC Technologies for Practical Application

Development of PEFC Technologies for Commercialization Promotion

Research on Nano-materials for High Performance Fuel Cells *1

Fuel Cell Cutting-Edge Scientific Research Project *2

Development of Highly Durable LPG Reformers of Membrane

*1 To be merged to new project

*2 Operated by METI in 2005-2008

SOFC

Development of SOFC System Technology

Development of elemental technology for SOFC Systems

Hydrogen

Advanced Research on Hydrogen Storage Materials

Fundamental Research Project on Advanced Hydrogen Science

Development for Safe Utilization and Infrastructure of Hydrogen

Development of Technologies for Hydrogen Production, Delivery and Storage Systems

Code & Standards

Establishment of Codes & Standards for Hydrogen Economy Society

Total budget
29.6Billion JPY for FY2009

Demonstrative Research

Japan Hydrogen & Fuel Cell Demonstration Project *3

*3 Operated by METI in 2006-2008

Demonstration of Residential PEFC System for Market Creation

Demonstrative Research on SOFC

Hydrogen Storage on board is a Key

State-of-art of FCV: 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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Development of On-board Hybrid Tank

NEDO-Development of Technologies Hydrogen Production, Delivery and Storage System　2007～2011

Structure

MH

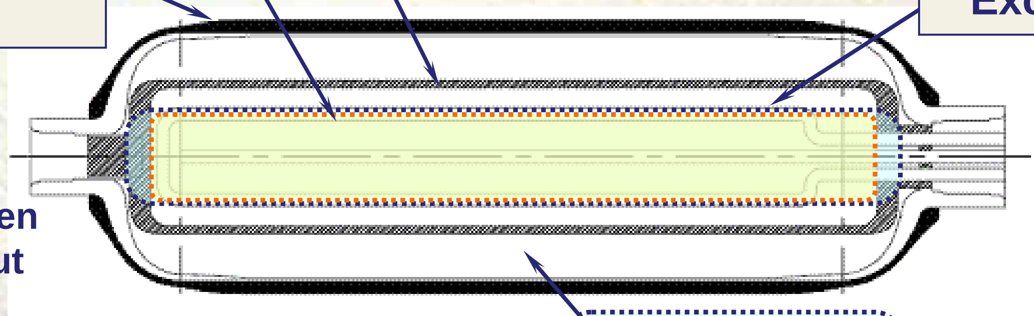
High Pressure Al CFRP Tank (type3)

MH Cartridge

Heat Exchanger

Coolant In& Out

Hydrogen In & Out



Compressed Gas 35MPa

2006 Proto-type

Combination of hydrogen storage materials (MH) and compressed gas

- High gravimetric hydrogen density
  1) Gravimetric H2 density > 3.0mass%　(1.8mass%,2006Proto-type)
  2) Volumetric H2 density > 34.5g-H2/L　(26g-H2/L,2006Proto-type)
  3) Recharge rate 90% / 5 min.
  4) Test of Safety performance
  5) Hydrogen storage alloy: BCCalloys
  6) Establish fabrication procedures

Comparison:24g-H2/L@70MPaTank

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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

HYDRO STAR

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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.

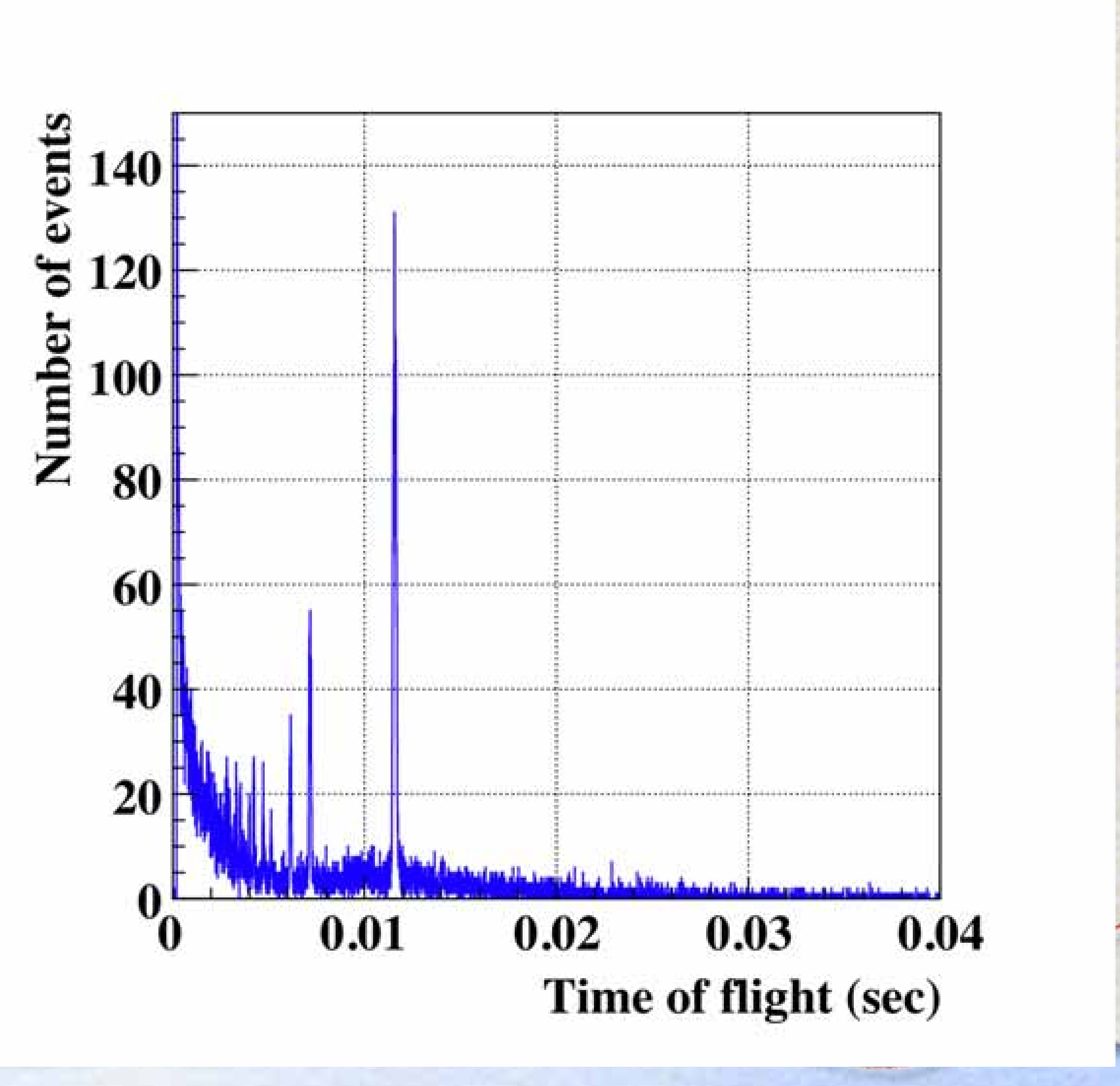
Total scattering = Bragg diffraction + diffuse scattering

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

The first data was successfully measured on 28 May 2009

Diamond
90 degree bank

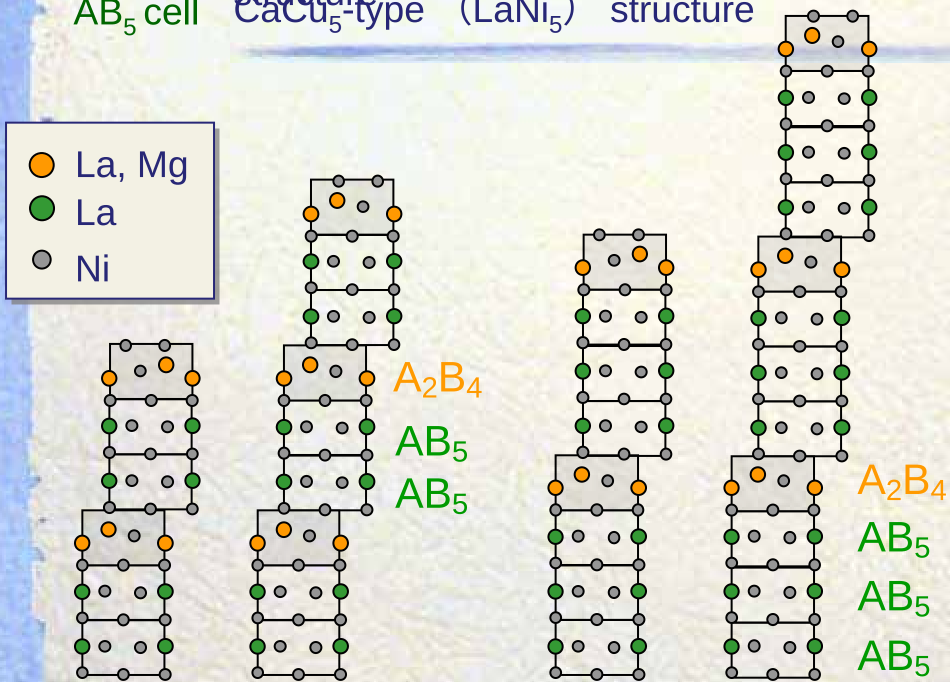


HYDRO STAR
AISI

A_2B_7， A_5B_{19} Alloys with Layered Structure

A_2B_4 cell MgZn$_2$-tupe structure （C14 Laves phase）

AB_5 cell CaCu$_5$-type （LaNi$_5$） structure



2H 3R 2H 3R

Ce_2Co_7 Gd_2Co_7 Pr_5Co_{19} Ce_5Co_{19}

$(La,Mg)_2 Ni_7$ $(La,Mg)_5Ni_{19}$

→ La_4MgNi_{19}

R & D for Ni-MH batteries
Kohno et al.J.Alloys Comp, 2000
$La_{0.7}\mathbf{Mg}_{0.3}Ni_{2.8}\mathbf{Co}_{0.5}$

Commercialized for ‘**eneloop**’ (SANYO Co. Ltd.)

$La_{0.7}\mathbf{Mg}_{0.3}Ni_{3.3}\mathbf{Al}_{0.1}$

$Mm_{0.83}\mathbf{Mg}_{0.17}Ni_{3.1}\mathbf{Al}_{0.2}$

Possibility to design materials because they consist of two units

↓

As the first step, hydrogen position in the lattice has been investigated

Hydrogenation of $La_2Ni_7$and structure change

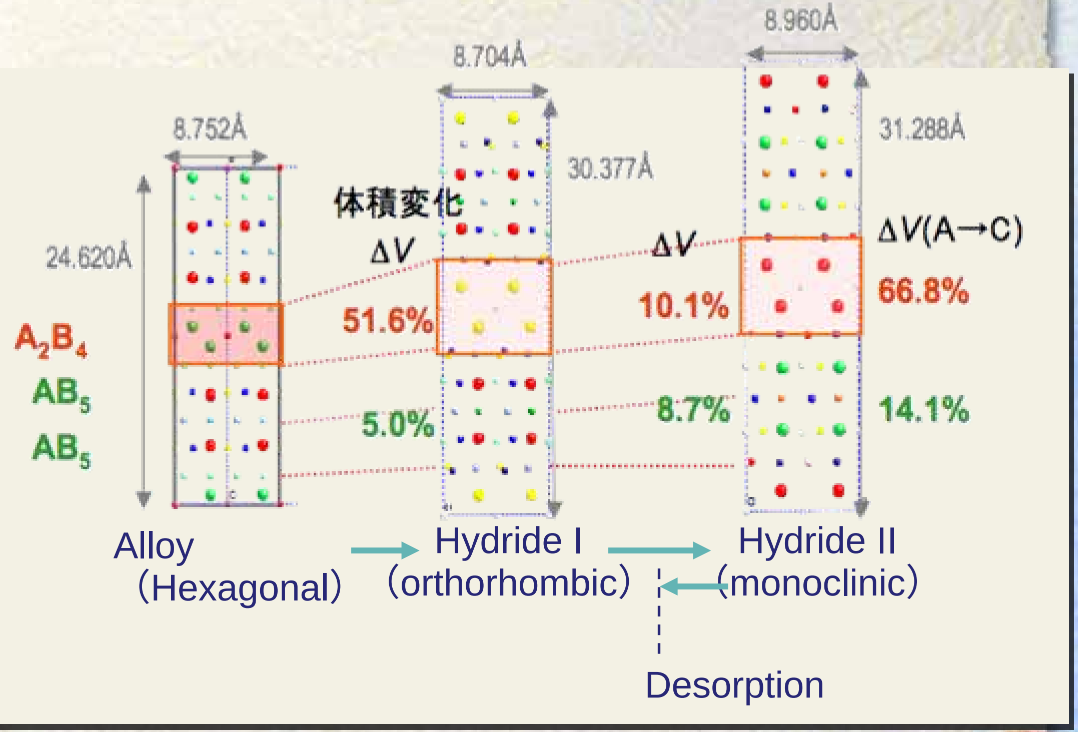
K. Iwase et al., to be published

In-situ X-ray diffraction measurement along p-c isothems

・Hydrogen only occupies A2B4 cell

・Because it is stable, hydrogen was not desorbed at room temperature

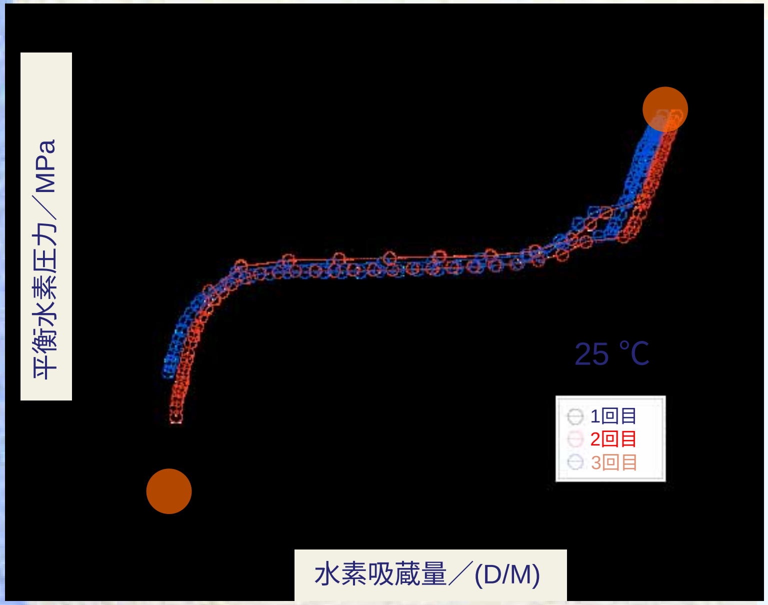
・Expansion along c-axis

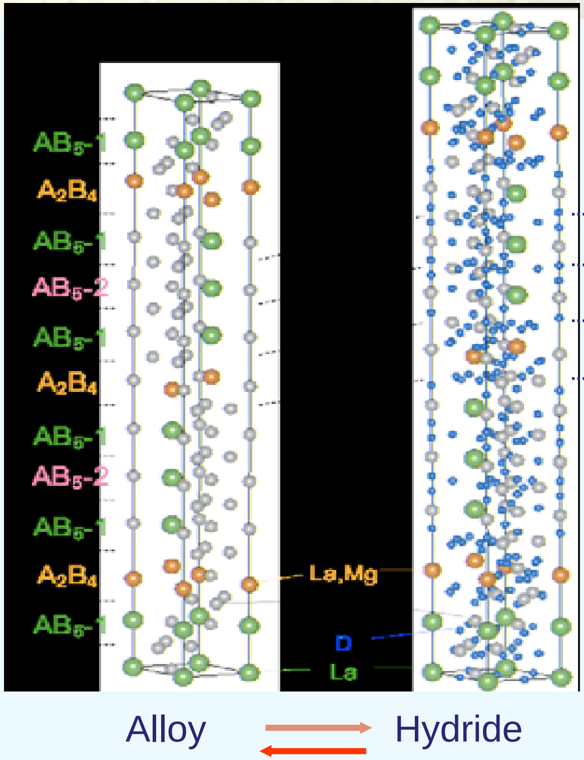


Structure of La_4MgNi_{19} hydride and hydrogen occupation

In situ neutron diffraction result

- Crystal structure of A_5B_{19}-type hydride was determined
- Substitution of Mg for rare earth has been clarified





- Hydrogen occupies almost same in numbers
- Isotropic expansion

Mg substitution makes almost same hydrogen occupation for the possible sites

J. Nakamura et al., J. Phys. Chem. C (2009)

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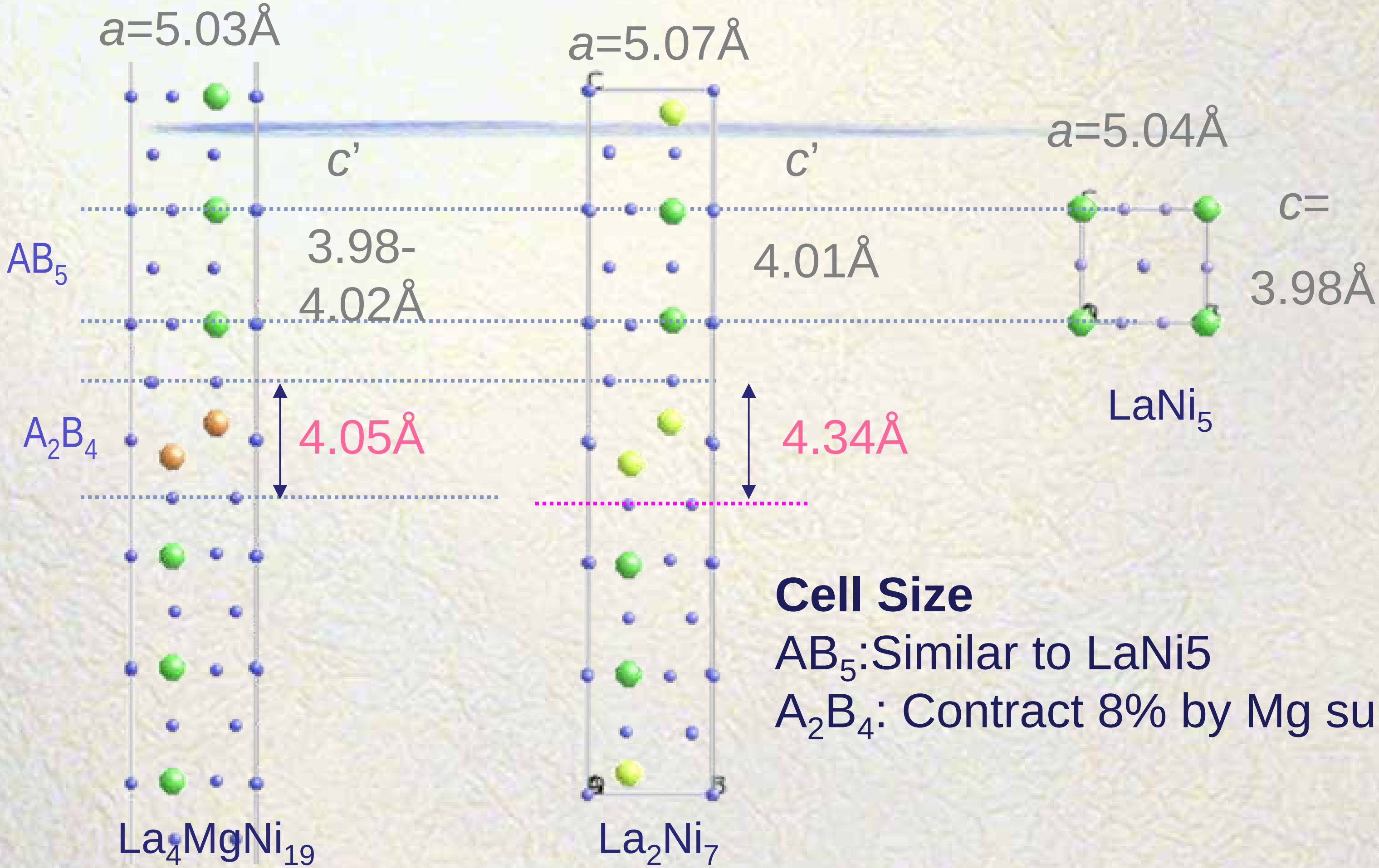
Mechanism：Contraction of A2B4 cell by Mg substitution

→ Stability of the site in A2B4 cell becomes similar to that of A2B5

Effect of Mg substitution for Rare earth



Cell Size

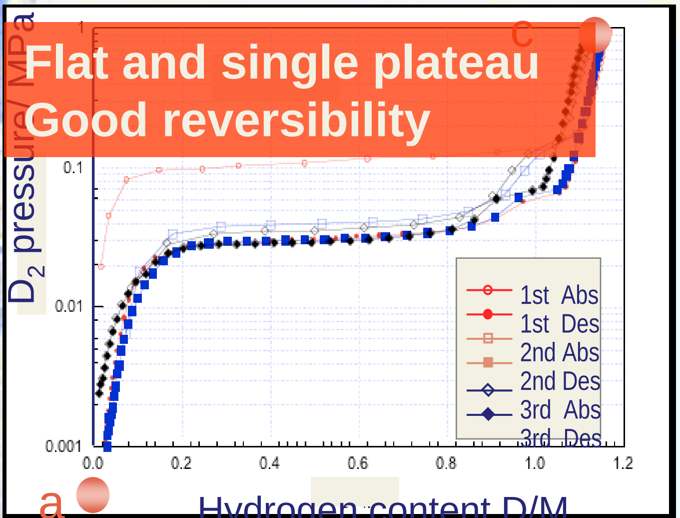
AB_5:Similar to LaNi5

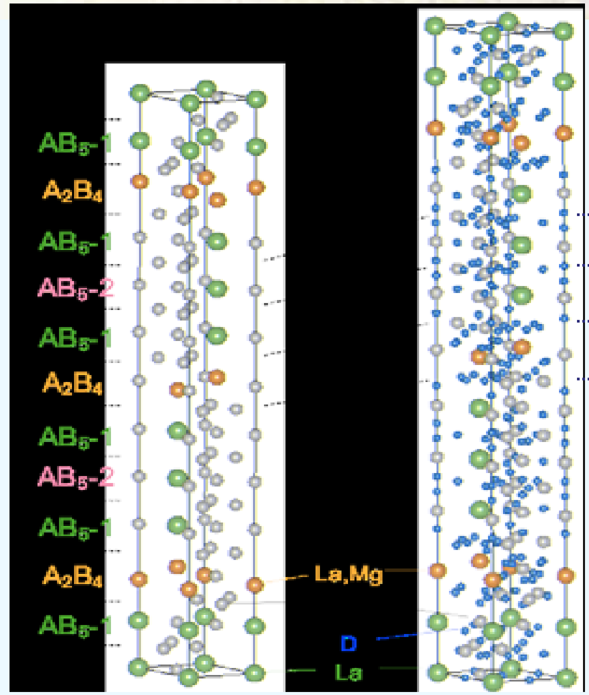
A_2B_4: Contract 8% by Mg substitution

A2B2 cell contracts by Mg substitution

→ That stabilizes the "A2B4 hydride"

Layered structure alloys：
Relation of hydrogenation and hydrogen occupation





	ΔV (%),	D/M
AB_5	22.2	1.04
AB_5	26.5	0.82
A_2B_4	25.8	0.98

Alloy ⇄ **Hydride**

Effect of Mg

Mg only substitutes A_2B_4 cell

- Contraction of **A_2B_4Cell**
- Destabilize hydride

Make balance the hydride stability of both cells

Hydrogen occupies every possible site equally

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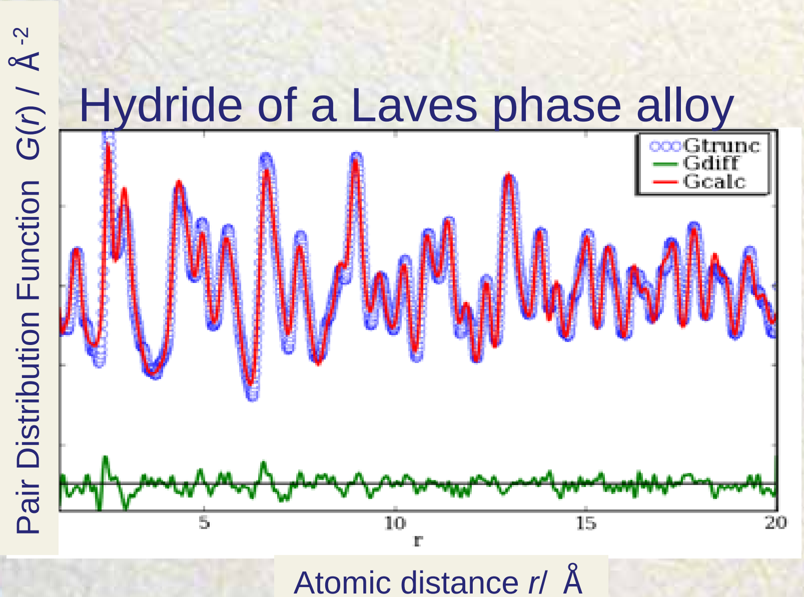
International Collaboration

Collaboration between Los Alamos National Laboratory, USA and AIST under the HYDRO-STAR

NPDF at LANSCE is powerful to analyze crystal structure and local structure of hydrides



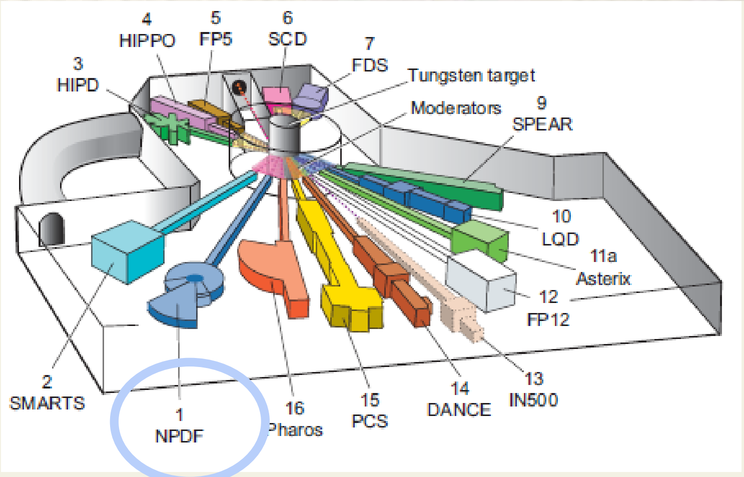


Fig. 3. The experimental hall with target, moderators, and instrumented flight paths in the Lujan Center.

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International Collaboration

- AIST initiated "Japan-China Seminar on Hydrogen Storage Materials" in 2006.
- China has started 937 Project on Fundamentals of Hydrogen Storage Materials since September 2009.

The 4th Seminar held in Guangzhou, China In April 2009.

Summary

- Japan has **National scenarios of market creation for fuel cells**.
- Commercialization of residential fuel cell has started this year.
- Commercialization of fuel cell vehicle is expected to start in 2015.
- Under these scenarios Japan is conducting R & D programs from fundamentals to demonstration.
- **Fundamental research on fuel cell and hydrogen is conducted under the Back to Basic policy.**
- For materials development, fundamental research utilizing large scale facilities such as neutron scattering and synchrotron radiation and collaboration experimental and computational science is significantly important.
- **International collaboration** is a key to establish hydrogen infrastructure.