For 8th IPHE ILC, Seoul , Korea (June 12-13, 2007)

Overview of Hydrogen Production and Storage Projects in Hydrogen Energy R&D Center

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Overview

I. Introduction

II. Current Hydrogen R&D Projects and Recent outputs

II. Summary

HERC

(Hydrogen Energy R&D Center)

www.h2.re.kr

- **Role**

  - Planning and managing the National Hydrogen production and
  Program supported by MOST

  *** 21st Century Frontier Program**

- **R&D Period**

  01 Oct. 2003 ~ 31 March 2013 (9.5 years for 3 phases)

- **R&D Fund**

  Total 111billion KRW (1000KRW=1 US dollars)
  (Government : 95 billion KRW, Industry : 16 billion KRW)

- **Sponsoring Ministry**

  Ministry of Science & Technology, Republic of Korea

Source: www.h2.re.kr

R&D Activities in the Phase II (HERC)(2006-2009)

	Action type	
Hydrogen Production		
▸ NG steam reforming for hydrogen station	(AR/DE)	(Mid)
▸ Biological hydrogen production	(BR/AR/DE)	(Long)
▸ Thermo-chemical hydrogen production	(BR/AR/DE)	(Long)
▸ Photocatalytic and photochemical hydrogen production	(BR/AR/DE)	(Long)
▸ Water electrolysis using PEM and THE	(BR/AR/DE)	(Long)
Hydrogen Storage		
▸ Hydrogen storage using metal hydrides	(BR/AR/DE)	(Long)
▸ Hydrogen storage using nano-structured materials	(BR/AR/DE)	(Long)
▸ Hydrogen storage using chemical hydrides	(BR/AR/DE)	(Long)
Hydrogen Utilization		
▸ Linear power/generation system of hydrogen combustion	(AR/DE)	(Long)
▸ Hydrogen sensor	(AR/DE)	(Long)

Supporting Project

- Measurement techniques for hydrogen storage materials
- Policy and technology assessment

BR: basic research, AR: applied research, DE: demonstration

P1. Compact NG steam reforming system for H_2-fueling station

❖ R&D Objectives

- Integrated design & development of on-site hydrogen production unit by steam reforming of methane
- Capacity: $20 m^3/hr$, Total production efficiency : 60%(LHV basis)

❖Content of R&D Activities

Hydrogen refueling station in KIER

- Location: KIER, Daejeon (Onsite SMR)
- Operation Pressure: 350 bar
- Storage Capacity: $170 m^3$
- Production Rate: $20\ m^3/hr$
- Open on August 25th, 2006

Project Manager: Dr. Yoon,Wang-Lai
wlyoon@kier.re.kr

P2. Biological Hydrogen Production

❖ R & D Objectives

-Scale-up and optimization of fermentative H_2 production process and development of bio-mimetic H_2 production system

Fermentative bioreactor scale : > 500 L

Fermentative H_2 productivity : 15 Nm^3 H_2/day/m^3

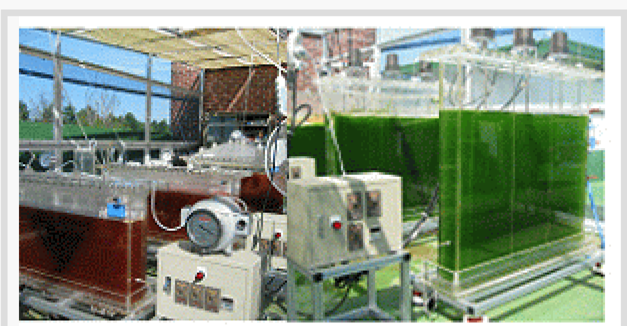
H_2 productivity by bio-mimetic system : 40 L H_2/kg protein/hr

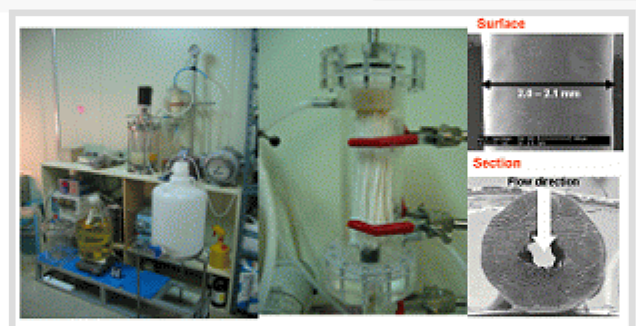
❖ Recent publications:

Int.J.Hydrogen Energy,31(2006)812-816

Int.J.Hydrogen Energy,31(2006)121-127

Korea Patent 2005-0032480





Bioreactors for photosynthetic and fermentative H_2 production

Project Manager: Dr. Kim, Mi-Sun,
bmmskim@kier.re.kr

P3. Photocatalytic and Photoelectrochemical Hydrogen Production Technology

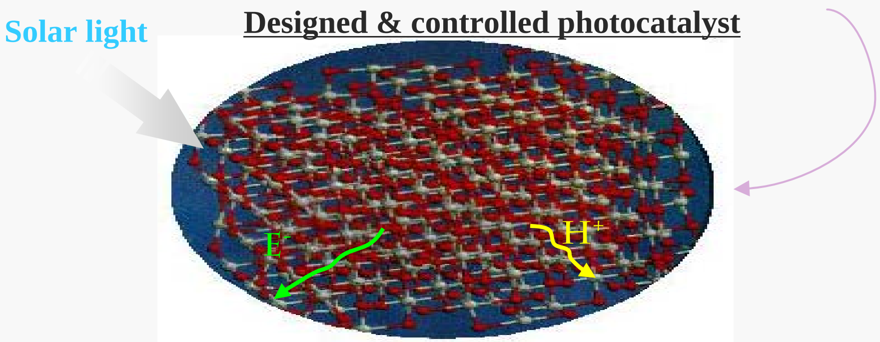
❖ R&D Objectives

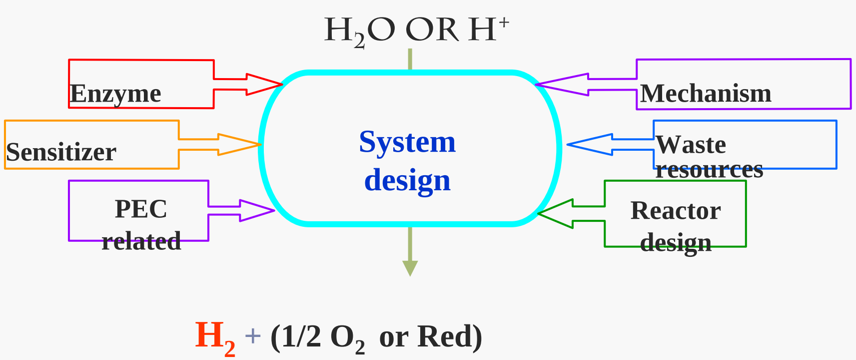
- **Development of the system for 3% solar light conversion efficiency (@AM 1.5) utilizing solar light-sensitizing photocatalyst**
- **System establishment for PEC cell of 7% efficiency**

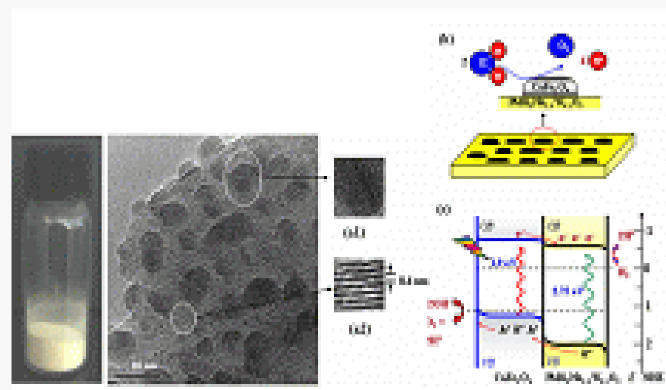
❖ Content of R&D Activities

- Highly active water splitting photocatalysts- material design
- Tandem-type photoelectrochemical cell modules
- PEC cell of 7% efficiency
- Photo/Biocatalyst
- Q-sized photocatalysts and mesoporous media
- Layered Perovskite and Composite Photocatalysts

KRICT, KIER, KIST, POSTECH, Nanopac





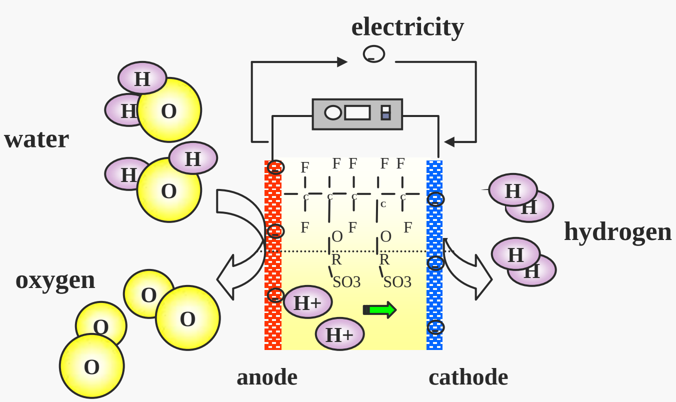


If any question, contact: Dr. Moon,Sang-Jin
moonsj@krict.re.kr

P4. Hydrogen production by electrolysis

❖ Contents of R&D Activities

- PEM electrolysis



Membrane-Electrode Assembly

- High temperature electrolysis (HTE)

Anode = $O^{2-} \rightarrow 1/2O_2 + 2e^-$

Cathode = $H_2O + 2e^- \rightarrow H_2 + O^{2}$

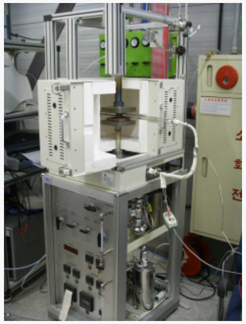
❖ R&D Objectives

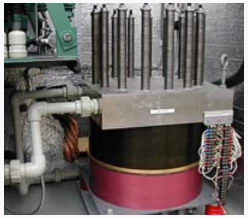
- Demonstration of $3Nm^3/h$ class PEME(Polymer Electrolyte Membrane Electrolysis) system
- Development of 50 L/h class HTSE(High Temperature Steam Electrolysis) stack

❖ Recent Publications:

Journal of Power Source, 149(2005)84-89

Korea Patent 2005-16642





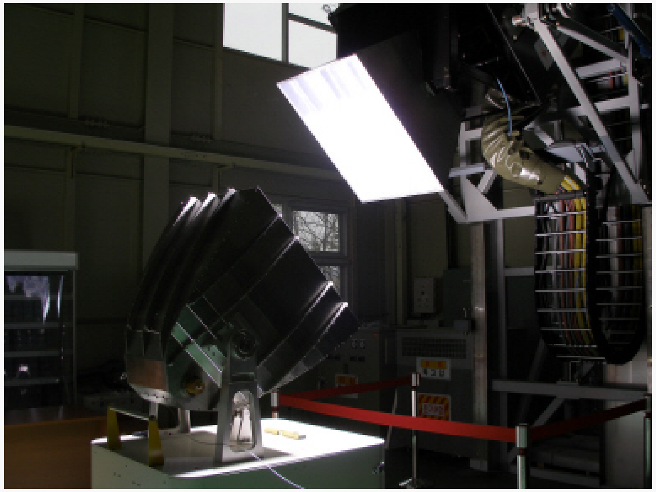
For more information, see: http://www.elchemtech.com/

P5. Hydrogen Production by Thermochemical Water-Splitting

❖ R&D Objectives

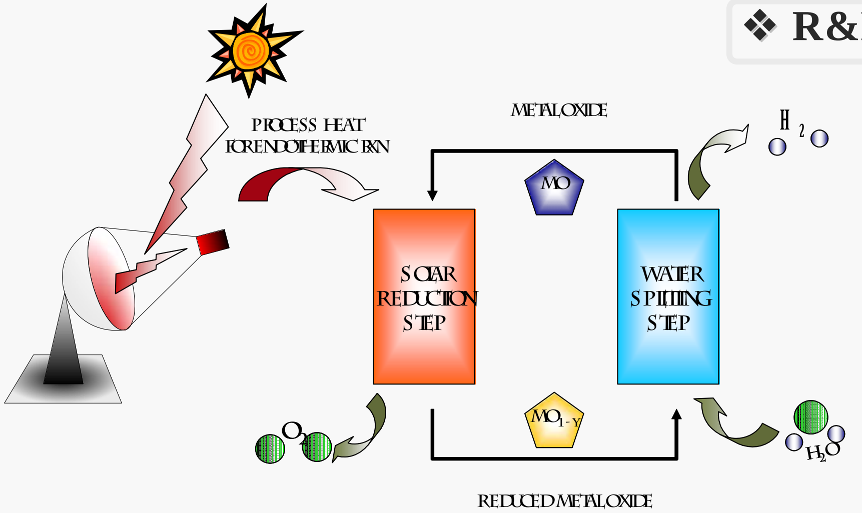
- Development of 2-step thermochemical hydrogen production system

➢Demonstrate lab. scale two-step thermochemical water splitting by the solar simulator system
➢Optimize the properties of the media
➢Improve the thermal stability of media and kinetics of water splitting reaction



300kW solar simulator and concentrator

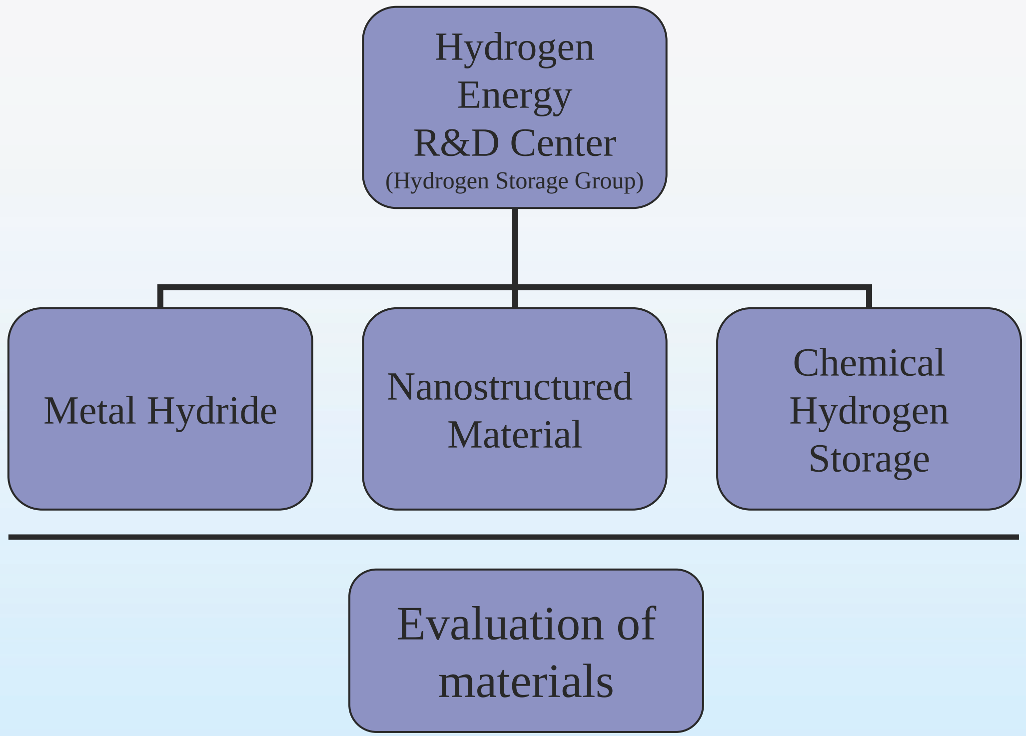
❖ R&D Scheme



❖ Recent Publications:
J.Ind.Eng.Chem., 10(6), 2004
IEEE transactions on Magnetics, 41(2005)
Korea Patent 0526052

If any question, contact: Dr. Chu-Sik Park , cspark@kier.re.kr

Strategy: Diverse Portfolio with Materials Focus



- Systematic approach
  - ✓Theory and experiment
  - ✓Independent analysis
- Universities, companies, Gov-led research institute
- Flexibility -Annual solicitation
- Close coordination with basic science and other agencies

S1. Chemical Hydrogen Storage

❖ R&D Objectives

- Development of a highly efficient hydrogen storage and generation system using NaBH4 and other chemicals

◈ Research outputs

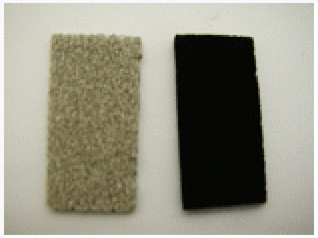
Development of high performance ceramic catalyst for $NaBH_4$ hydrolysis ..

Development of hydrogen reactor operated at room temperature and atmospheric pressure.

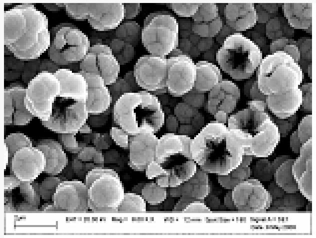
Development of coating technology of the ceramic catalyst

❖ Content of R&D Activities

H_2 Storage Technology	H_2 Release System for Mobile Uses
· $NaBH_4$/$NaBO_2$ Recycling Technologies · Reactor Development	· H_2 Release System · Catalyst Development
Samsung Engineering, KIST, University	



Co-B catalyst coated on Ni foam



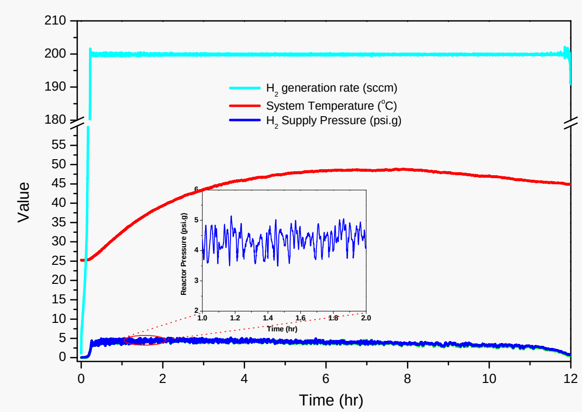
Porous Co-P catalyst

If any question, contact: Dr. Yu,Yong-Ho
yongho.yu@samsung.com

Characteristics of the hydrogen generation system

- Bellows type batch reactor
- Self-regulating system by pressure control
- Constant supply of Hydrogen
- System without a pump
- Operation at room temperature and atmospheric pressure

Patent pending	
domestic	foreign
7	3

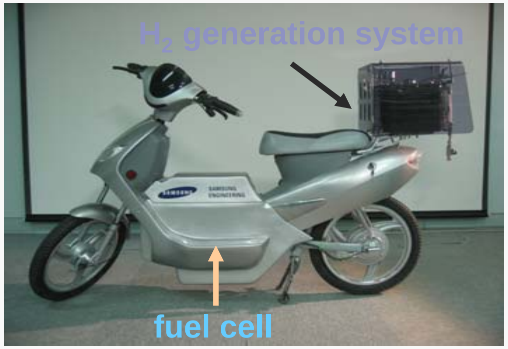


Demonstration of the system operations

Energy density of the system : 50 kg/m^3

- Setting up the fuel cell operation tester with a hydrogen generation system
- Development of modular hydrogen generation system for 100W and 1KW

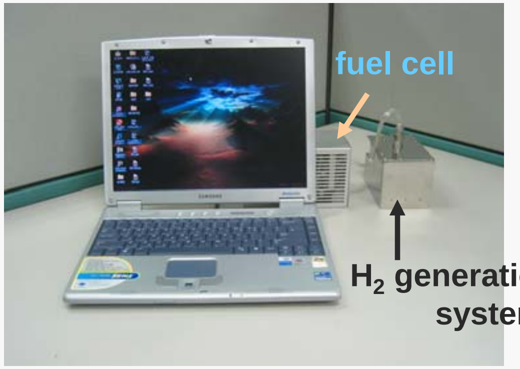
◈ Fuel cell scooter operated by a H_2 generation system using $NaBH_4$



@ 300W fuel cell system

@ The scooter can run up to 140 kilometers on 6 liters of hydrogen fuel

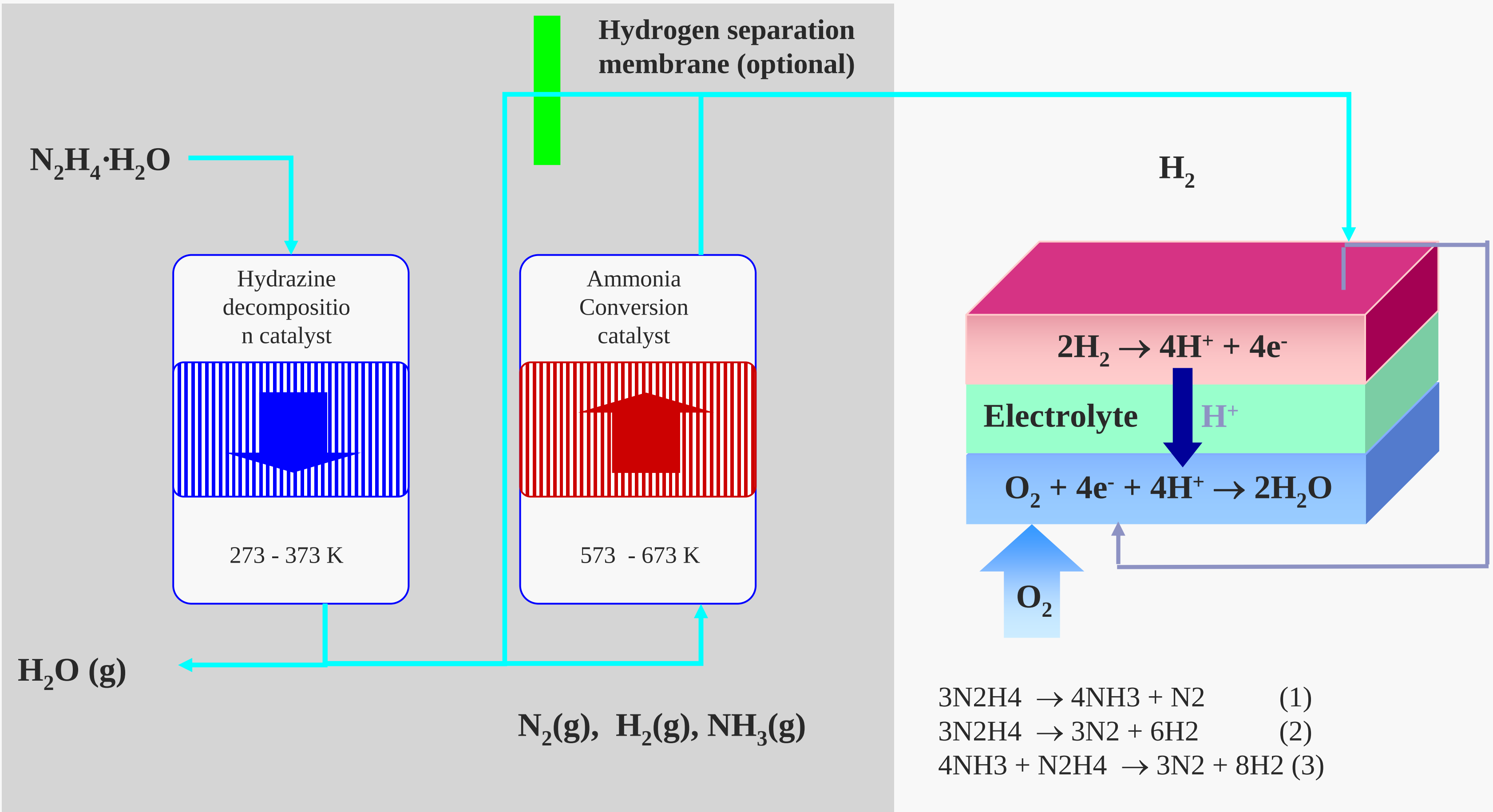
◈ Fuel cell notebook operated by a H_2 generation system using $NaBH_4$



@ 20W fuel cell system

@ Ceramic catalyst was used

Hydrazine hydrate decomposition system



3N2H4 $\rightarrow$ 4NH3 + N2 (1)
3N2H4 $\rightarrow$ 3N2 + 6H2 (2)
4NH3 + N2H4 $\rightarrow$ 3N2 + 8H2 (3)

$$3N_2H_4 \cdot H_2O\ (l) \rightarrow 4(1-x)NH_3\ (g) + (1+2x)N_2(g) + 6xH_2(g) + 3H_2O(g)$$

S2. Metal Hydride Hydrogen Storage

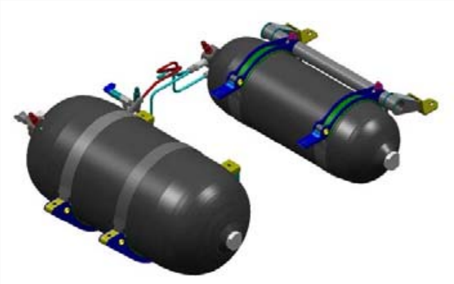
❖ R&D Objectives

- Develop metal hydride hydrogen storage materials and storage system for fuel cell vehicle (FCV)

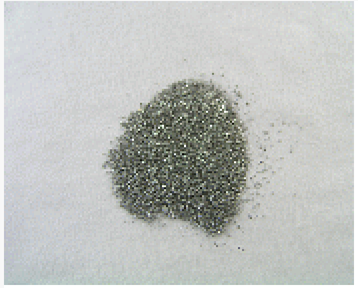
❖Content of R&D Activities

Basic research of metal hydride hydrogen storage systems for a fuel cell vehicle

- High-performance hydrogen storage material using metal hydrides, with design technology for hydrogen storage vessels thereof
- Preparation of alkali-metal complex hydrides for hydrogen storage



High pressure hydrogen gas tank system



Hydrogen storage material

-Metal hydride hydrogen storage system
For a fuel cell vehicle
-metal hydride
-alkali metal complex
- Mg based hydrogen storage material

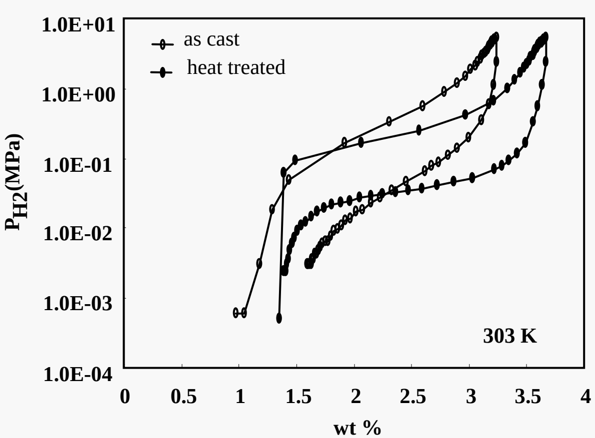
Results and Accomplishments: $Ti_{0.32}Cr_{0.43}V_{0.25}$ Alloy

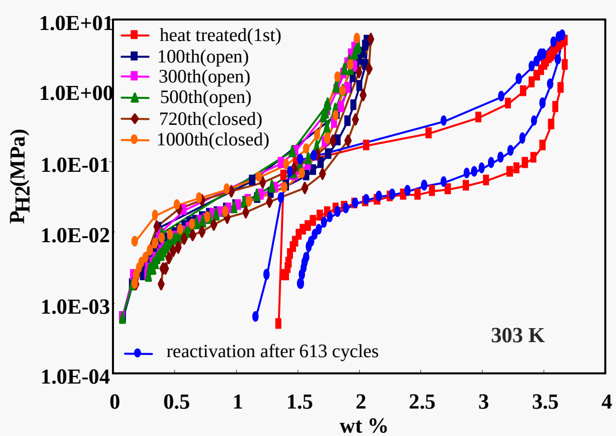
- **Improved effective hydrogen storage capacity**
  : 2.3 wt%(total 3.7wt%) and 140kg of H_2/m^3
  (gravimetric and volumetric values at 303K)

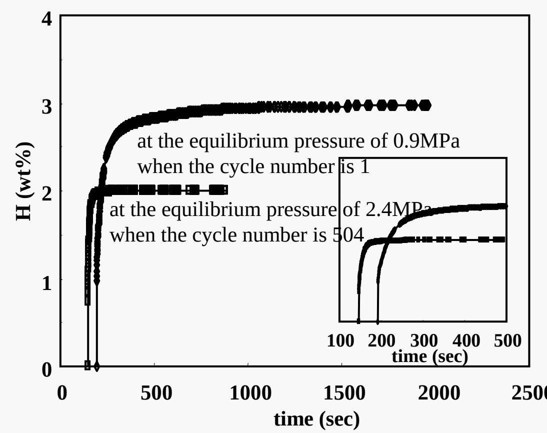
$Ti_{0.32}Cr_{0.43-X}V_{0.25}M_X$ ($0 \leq X \leq 0.10$, M=Mn, Fe) alloys

- **Excellent cyclic ability**
  : More than 2 wt% even after 1000 cycles of pressure swing cyclic tests

- **Excellent hydrogen absorption rate**
  : More than 95% is absorbed within the first 10 min of the first cycle and more than 98% within the first 2 min after a few cycles

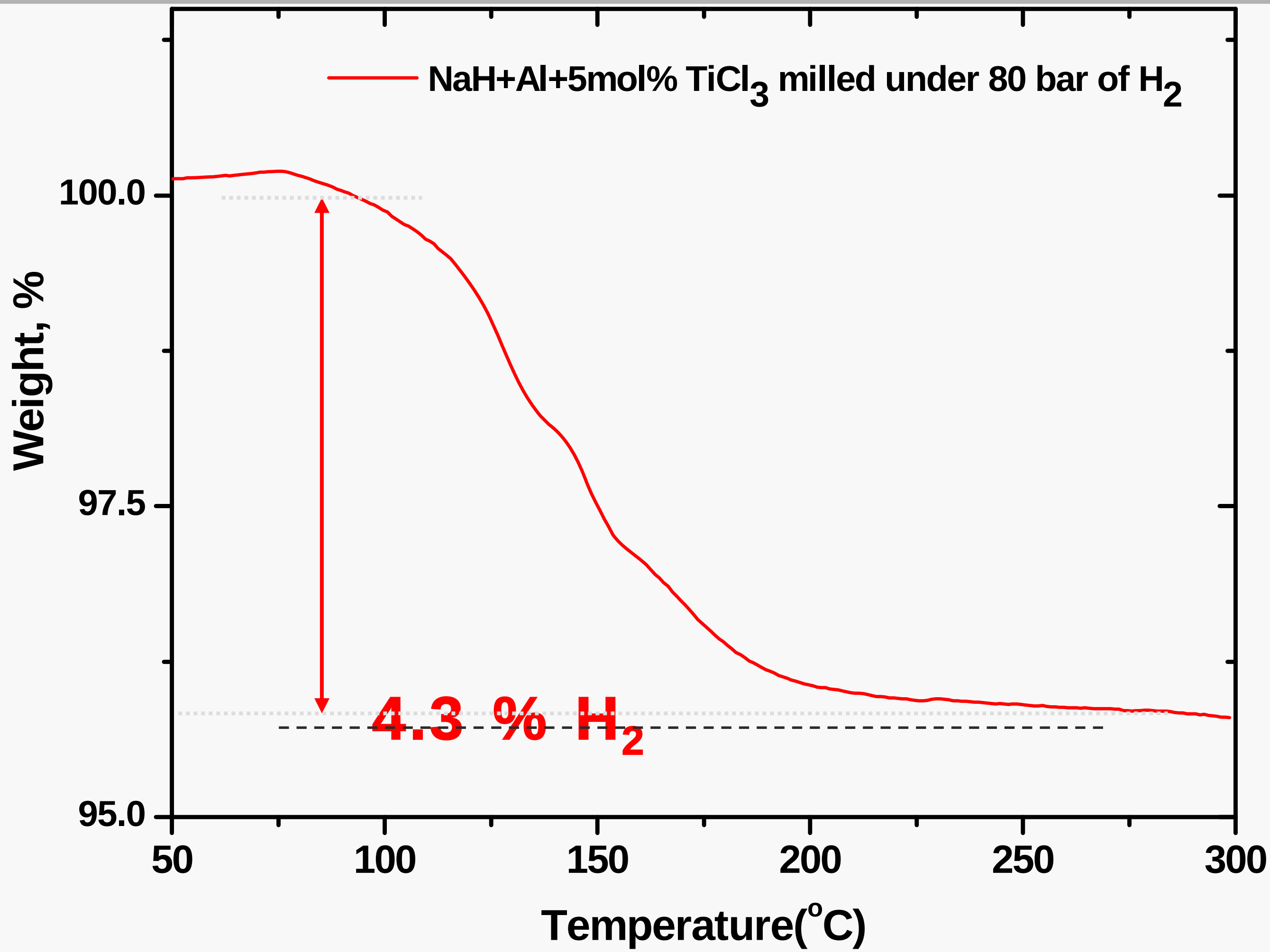




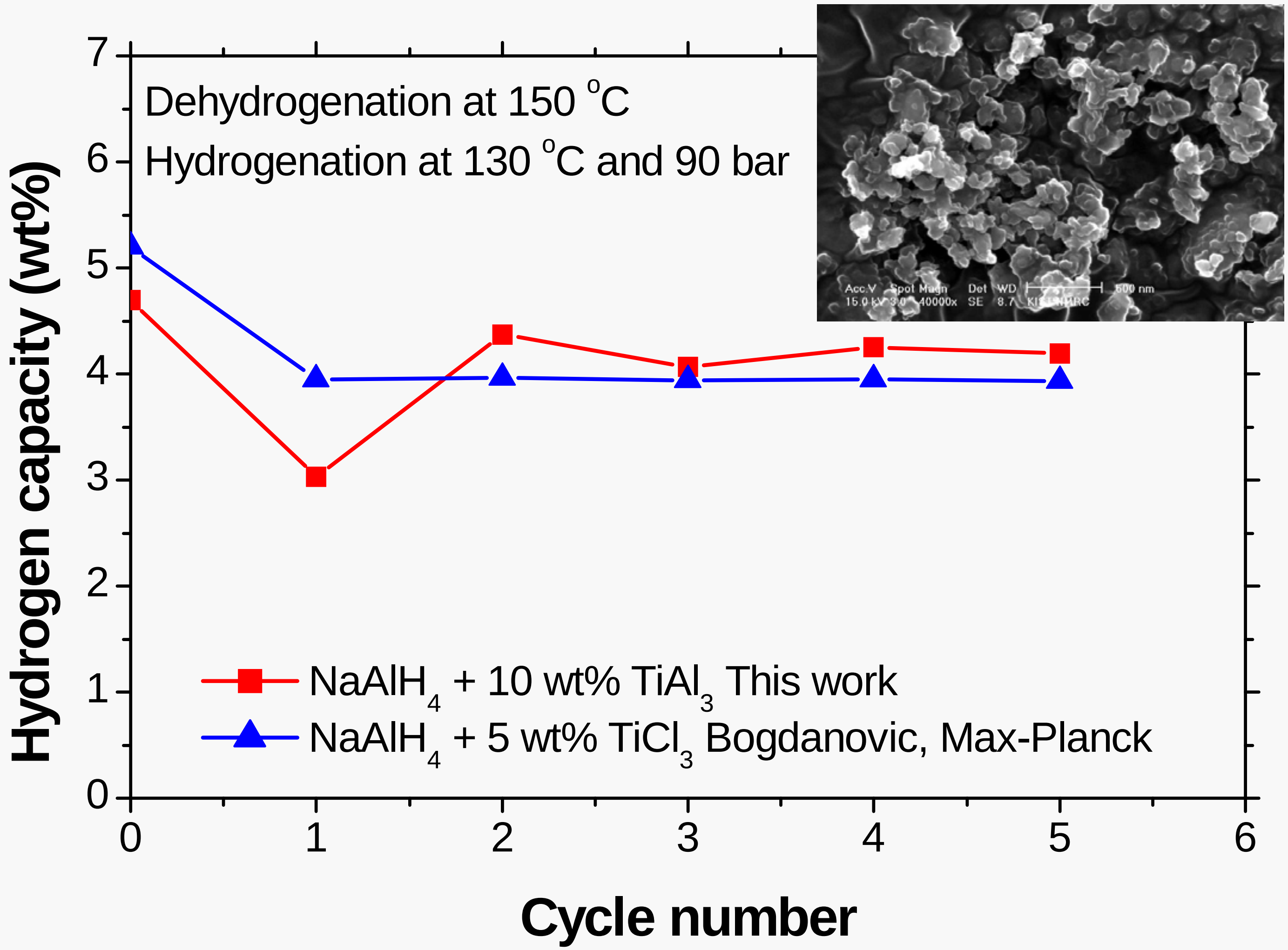


S. W. Cho, G. Shim, G.S. Choi, C.N. Park, J.H. Yoo and J. Choi, "Hydrogen absorption–desorption properties of Ti0.32Cr0.43V0.25 alloy ", J. Alloys Compd, 430: 136-141(2007)

Alkali-metal hydride- Improvement of storage capacity by reaction milling



Cycle performance of $NaAlH_4$ with nano-catalyst



S3. Porous nanostructured materials

❖ R&D Objectives

- Study on the nano-materials for hydrogen storage

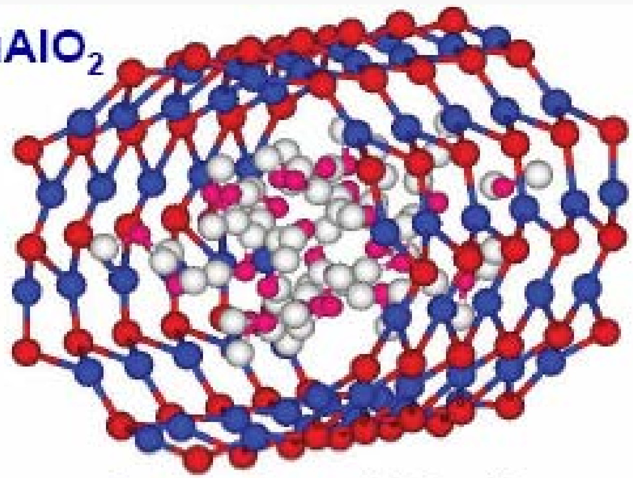
❖Content of R&D Activities

- High density porous carbon and metal/carbon composites
- Surface functionality of nanoporous carbon for hydrogen storage
- Hydrogen storage materials based on molecular crystals and metal-dispersed materials
- Synthesis of transition metal-dispersed nanotubes
- Optimized materials design using quantum simulations
- Search for new class of hydrogen storage materials: non-covalent bonded molecular crystals
- Characteristic Research of porous nanostructured materials based on molecular modeling

If any question, contact: Dr. Hae-Jin Kim, hansol@kbsi.re.kr

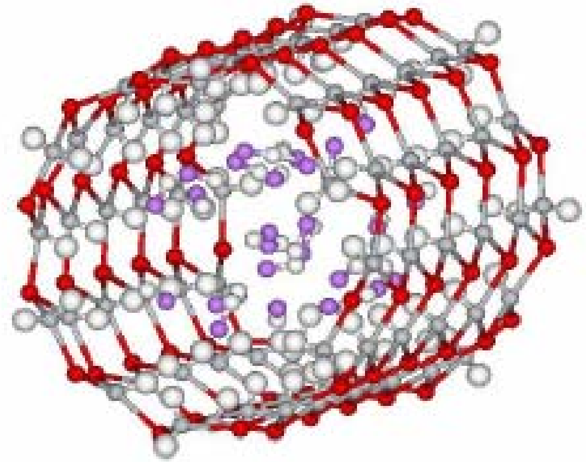
MD Simulation of H2 Storage in Metal Oxide Nanotubes

$CuAlO_2$



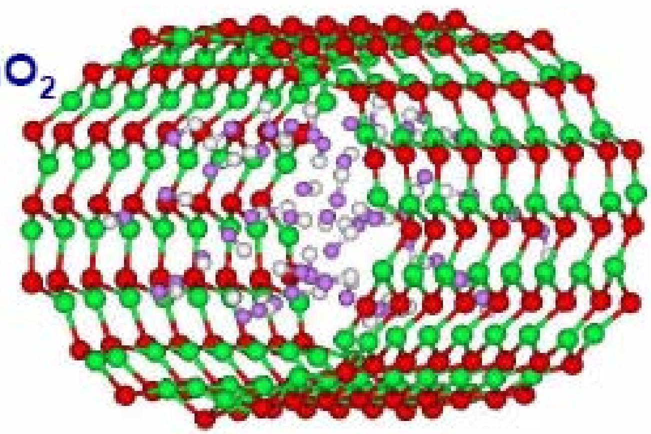
Surface Area : 1128 m^2/g

$LiTi_2O_4$



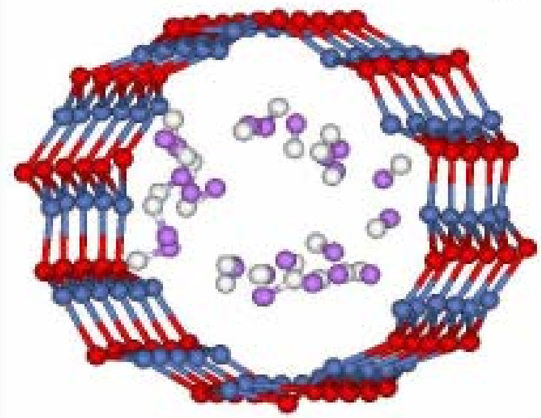
Surface Area : 1860 m^2/g

$LiMnO_2$



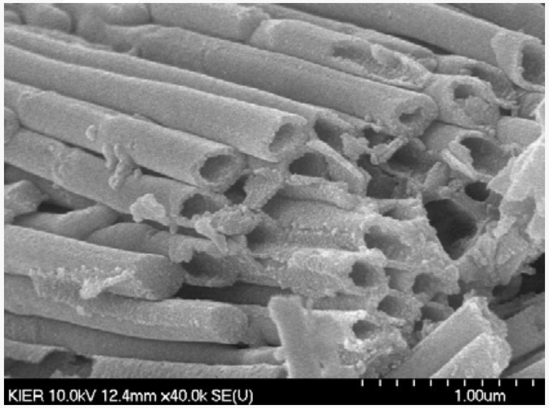
Surface Area : 2949 m^2/g

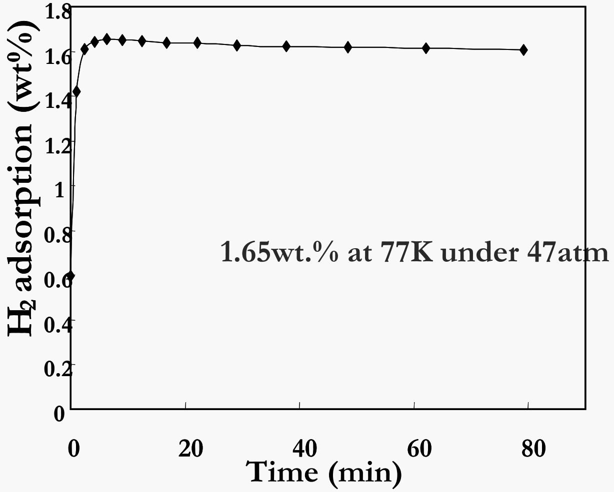
$LiNiO_2$



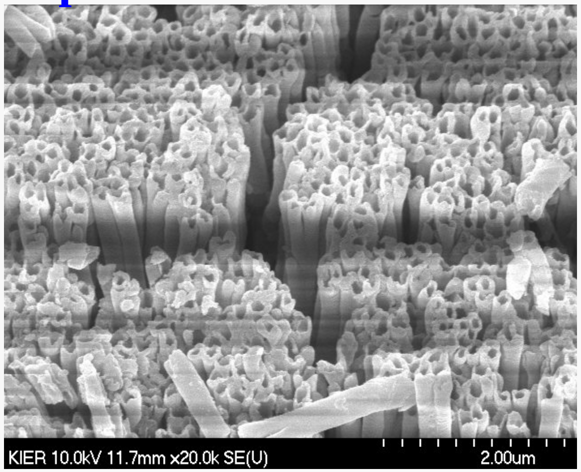
Surface Area : 1322 m^2/g

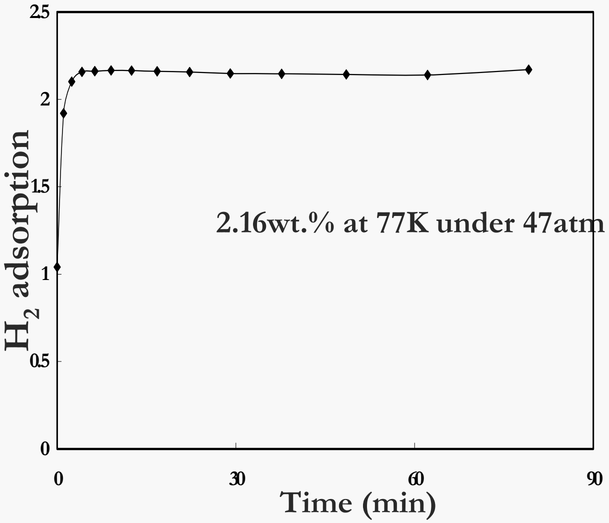
❑ Li-dispersed nickel oxide nanotubes



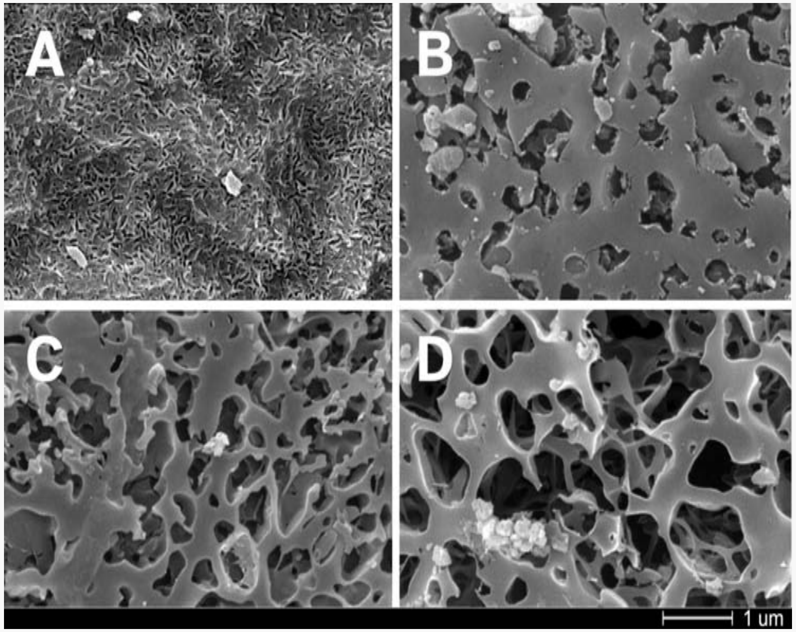


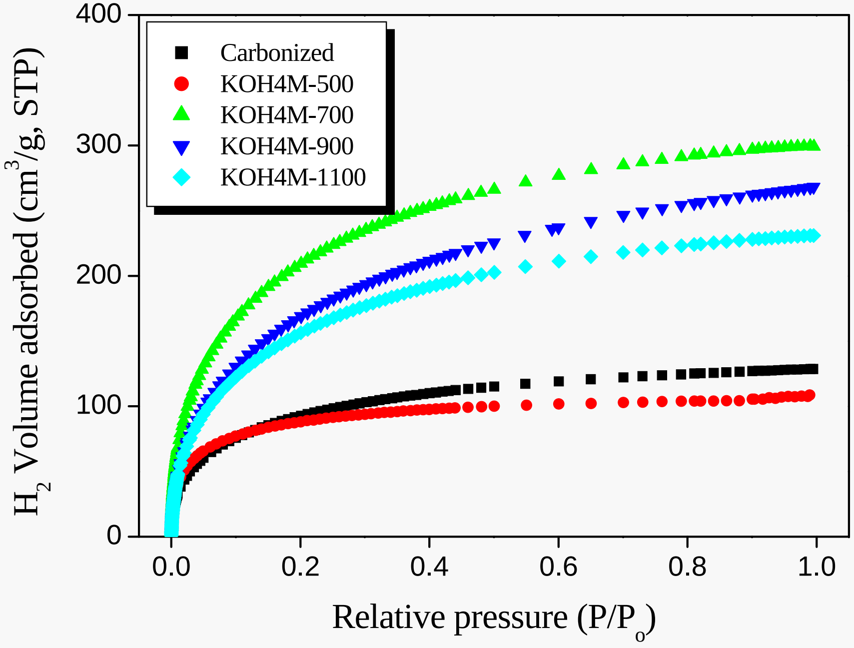
❑ Li-dispersed silica nanotubes





Carbon Molecular Sieves from Polymeric Precursor

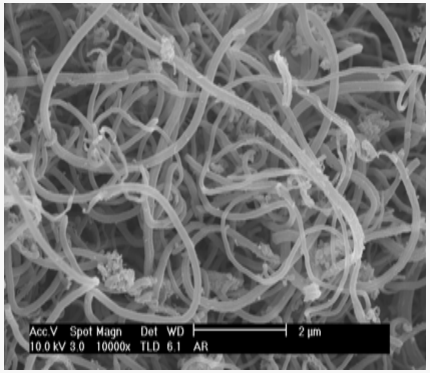




Pore size-controlled carbon molecular sieves;
(a) as-received, (b) KOH-1.0, (c) KOH-2.0,
(d) KOH-4.0

(H_2 adsorption at 77K)

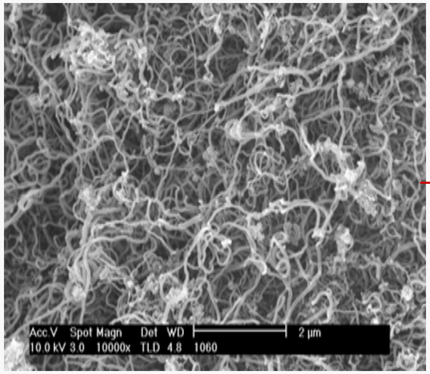
Preparation of Porous Carbon Nanofibers



(a) 2 μm

Porous carbon nanofibers were achieved by a physical activation method at 1000°C, resulting in obtaining over <u>2000 m^2/g of specific surface area</u>

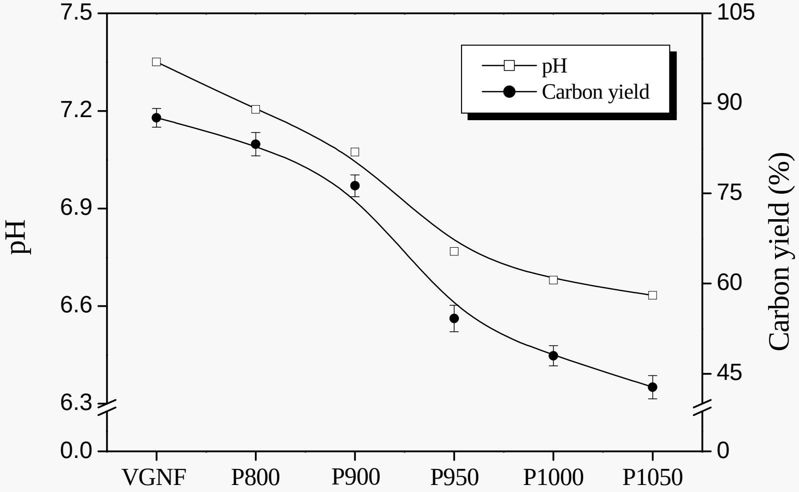
Nanotechnology **17**, 4395 (2006)



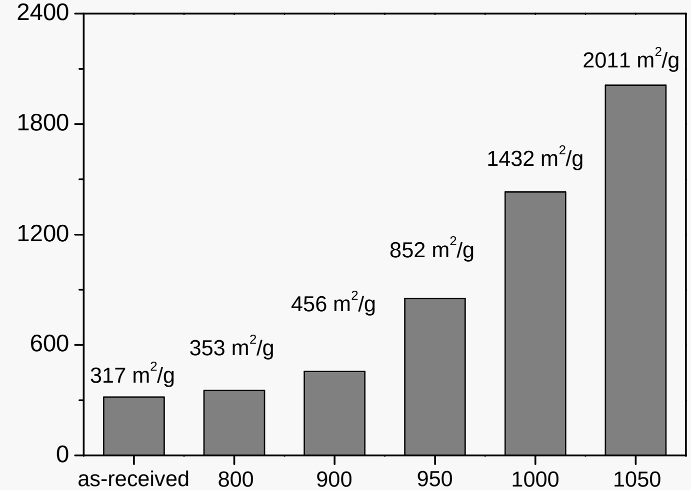
(b) 2 μm

(c) 500 nm

(a) as-received, (b) porous carbon nanofibers activated at 1050°C, (c) magnification of (b).

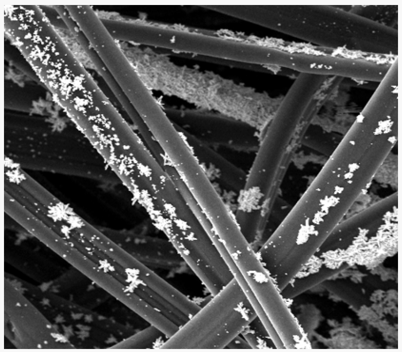


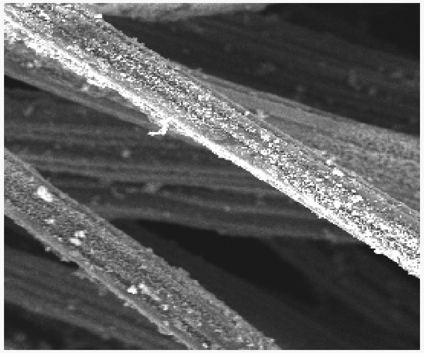
Surface pH and Carbon yield of porous carbon nanofibers

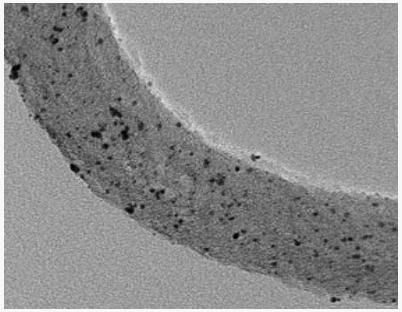


Specific surface area of porous carbon nanofibers

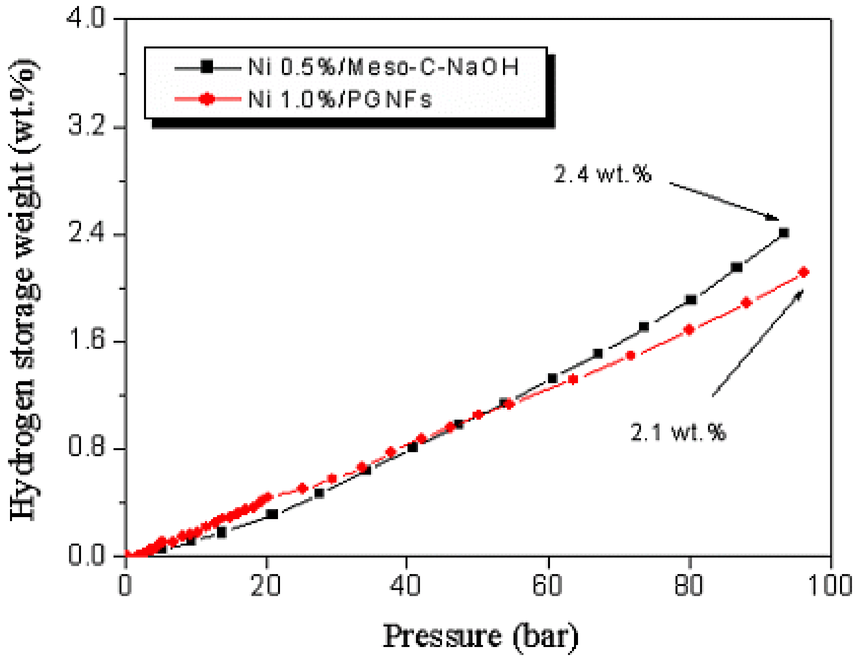
Nanosized Metal-loaded Carbon Materials







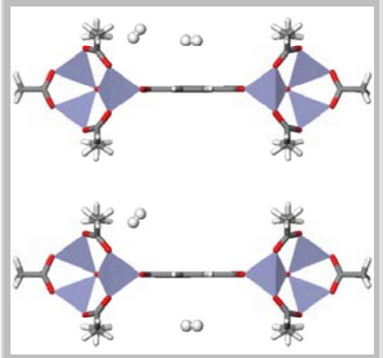
(a) Cu-plated activated carbon fibers, (b) Ag/Ni - plated activated carbon fibers, (c) electrolessly Ni-plated (2~5 nm of metal particle size)

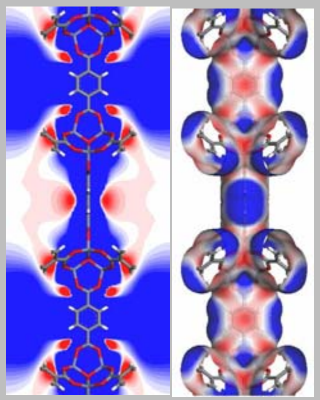


Hydrogen storage behaviors after transition metal loading

S4. New Material Search

Modeling





MOF

Organic zeolite

Synthesis

solution of terephthalic acid

solution of zinc source (e.g. oxide, nitrate)

precipitation, crystallization
temperature: 105 – 130 °C
time: 3 – 20 hours

filtration, drying

recycling solvent

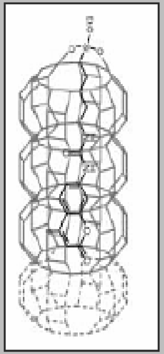
shaping

Synthesis of Zeolites
Zeolite X, Y, L, etc.

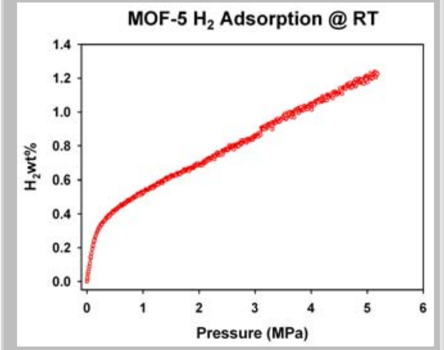
Adsorption of organic molecules
biphenyl, naphthalene, etc.

filtration, drying

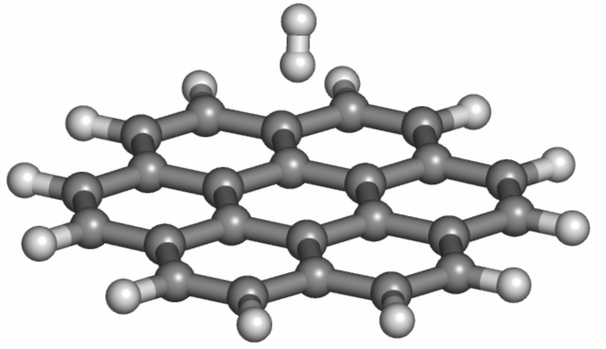
recycling solvent

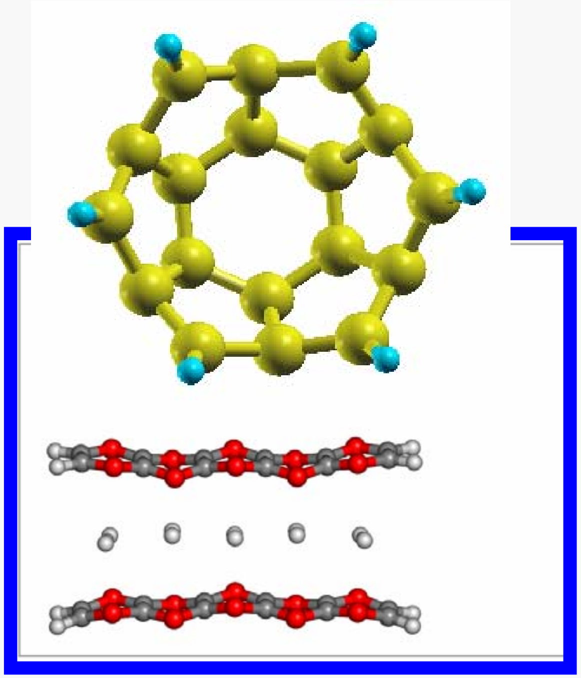


Evaluation



New building Blocks for Hydrogen Storages Based on Non-covalent Bonding





Selection rule and strategy

- Binding energy
- Structural characteristics
- Doping & structural changes
- Ab initio quantum simulations

Candidate materials

- Metal-dispersed nanostructures
- Molecular crystals

Target

- Design new materials based on non covalent bonding
- Optimize binding energy and ratio
- Metal dispersion without clustering

S5. Evaluation of Hydrogen Storage/Discharge Materials

- Measurement of hydrogen storage/discharge amount in various hydrogen storage materials (volumetric measurement method, gravimetric measurement method)
- Database of hydrogen storage materials
- Standardization of measurement methods for hydrogen storage/discharge materials

Volumetric (left)/Gravimetric (right) Measurement Equipments

HERC Budget

Activity	Funding (KRW in millions)			
	FY 2005 Approp	FY 2006 Approp	FY 2007 Actual	FY 2008 Request
Hydrogen Production	3675	4295	4415	
Electrolysis	600	810	840	
Steam Methane reforming	1060	600	630	
Biological	650	800	800	
Photochemical/PEC	860	1515	1575	
Thermochemical	505	570	570	
Hydrogen Storage	3230	3140	3199	
Metal hydride	1120	990	972	
Nanostructured material	1120	1300	1347	
Chemical Hydrogen Storage	535	550	550	
Evaluation	455	300	330	
Others	1870	1499	1751	
TOTAL	**8775**	**8934**	**9415**	

** Government side fund only*

For More Information

Hydrogen Production Groups	Hydrogen Storage Groups	Hydrogen Utilization Groups

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Thank you for your attention!

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