Special series on "Energy Materials"

1) Energy materials (1): One-dimensional inorganic nanomaterials	- Wed November 19, 2008 at 10:00
2) Energy materials (2): Advanced porous materials	- Mon November 24, 2008 at 10:00
3) Application of energy materials: Hydrogen energy and fuel cells	- Thu November 27, 2008 at 10:00

Yoshikazu Suzuki
Institute of Advanced Energy, Kyoto University

Advanced Energy Materials

(1) Energy Conversion Materials

Light ⇨ Electricity (photovoltaic: Si, CdSe, TiO_2...)
Heat ⇨ Electricity (thermoelectric)
Chemical ⇨ Electricity (battery, fuel cells...) etc.

(2) Energy Storage Materials

Li ion Battery, Hydrogen storage, ...

(3) Energy Transfer Materials

Superconductor, ...

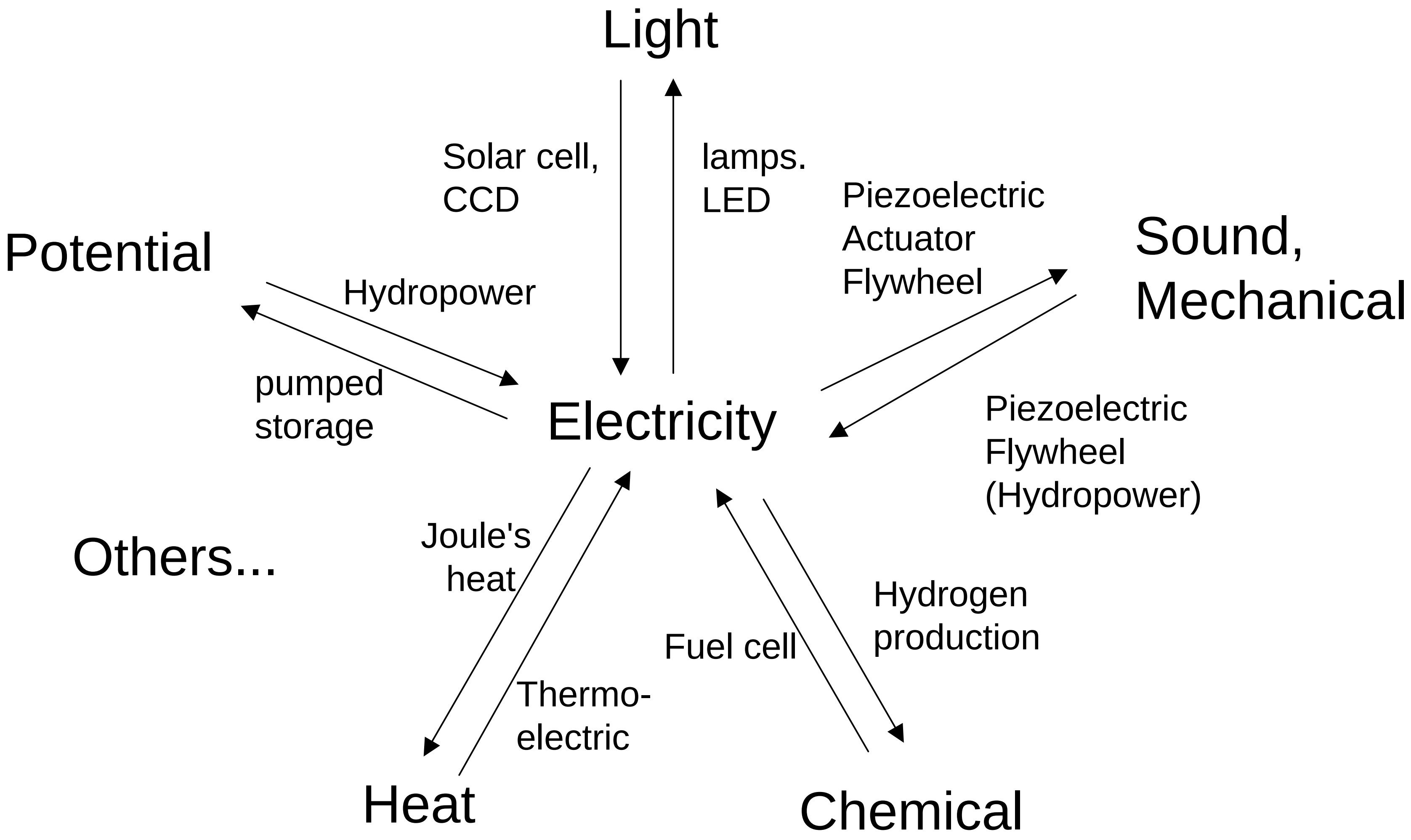
(4) Energy Saving Materials

High-temperature structural materials, ...

(5) Materials for Extreme Conditions

Nuclear fission, nuclear fusion etc.

Examples of energy conversion



Light

Solar cell, CCD

lamps. LED

Potential

Hydropower

pumped storage

Sound, Mechanical

Piezoelectric Actuator Flywheel

Piezoelectric Flywheel (Hydropower)

Electricity

Others...

Joule's heat

Thermo-electric

Fuel cell

Hydrogen production

Heat

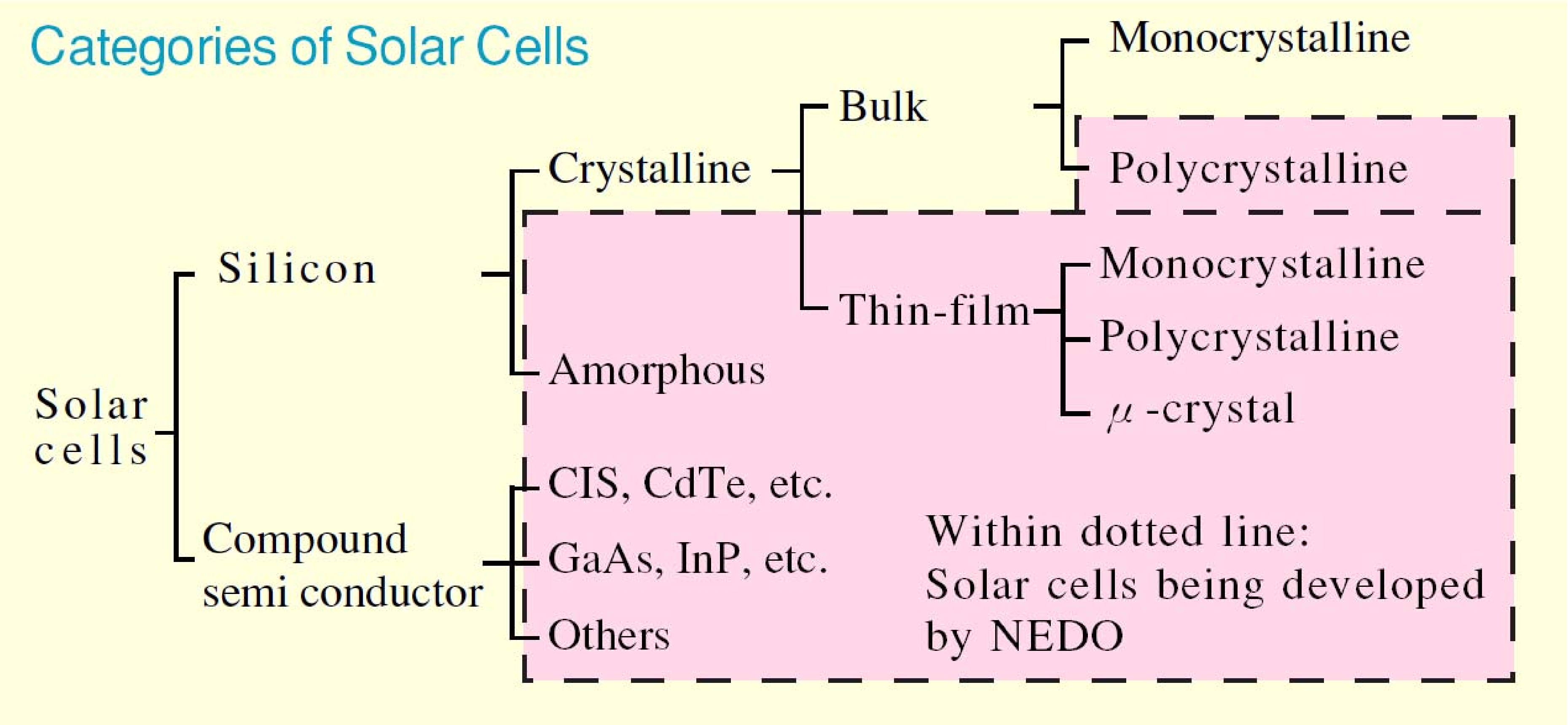
Chemical

Electricity is centered due to its "convenience" for engineering.
Electricity is a kind of "secondary energy"

Quiz "primary or secondary energy", storage

	primary	secondary	storage (Y/N)
Crude oil			
Electricity			
Solar heat			
Solar light			
Hydrogen			
Wind			
Natural gas			
Gasoline			
Biodiesel			
Geothermal			
Atomic			

Photovoltaic (Solar Cells) Power Generation Technology



Categories of Solar Cells

Within dotted line:
Solar cells being developed by NEDO

NEDO: The New Energy and Industrial Technology Development Organization

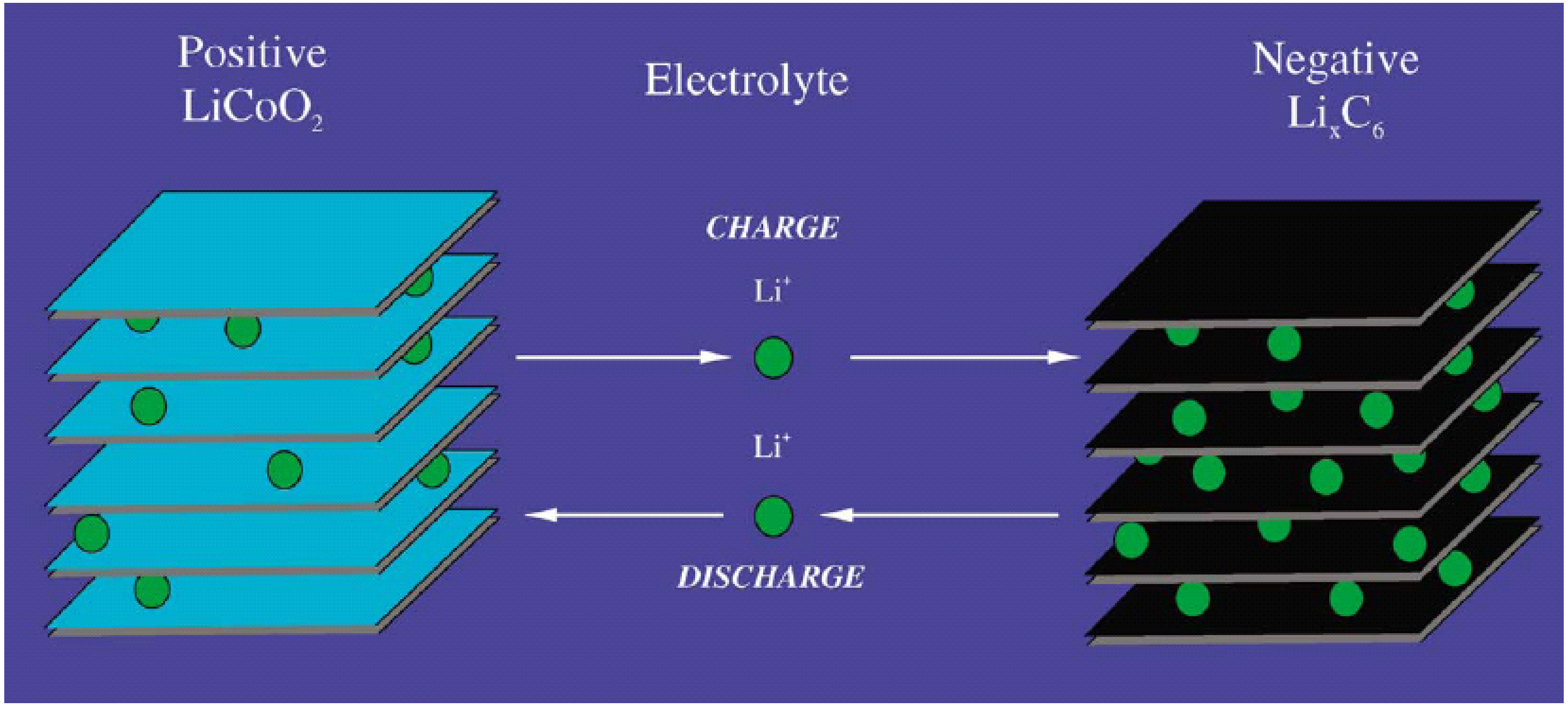
Establishment: October 1, 1980

Capital: ¥523.7 billion (as of September 2003)

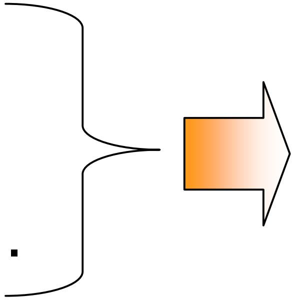
http://www.nedo.go.jp/

Energy Storage Materials

Schematic representation of a rechargeable lithium-ion battery.



Peter G. Bruce, Solid State Sciences, **7**, 1456 (2005).



- More Li ion
- Reversible,
- Cost, reliability, durability...

New materials

Energy Transfer Materials

Oxide superconductor tape > 500 m (YBCO)

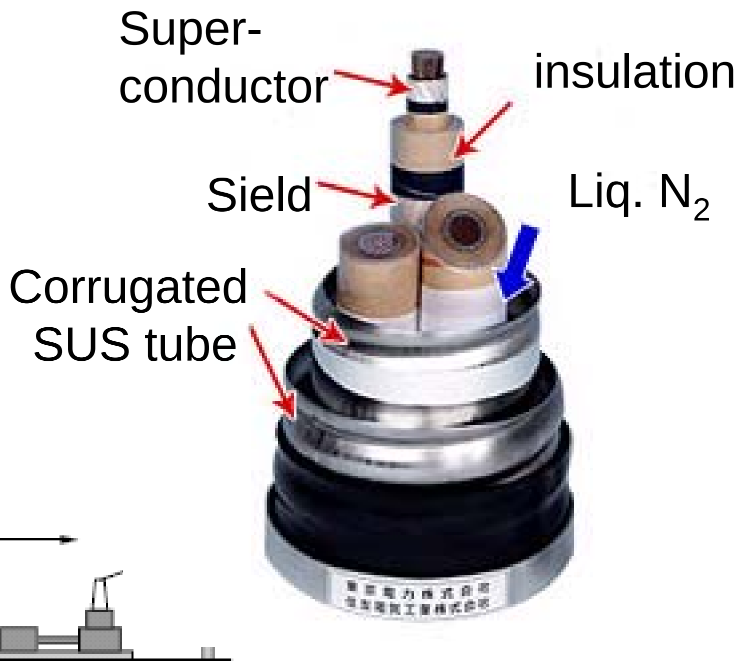
YBCO:
Y : Ba : Ca = 1 : 2 : 3

Fujikura Co., 2007

Energy Transfer Materials

Oxide superconductor tape > 1000 m (Bi2223)

Bi2223 : Bi : Sr : Ca : Cu =2:2:2:3



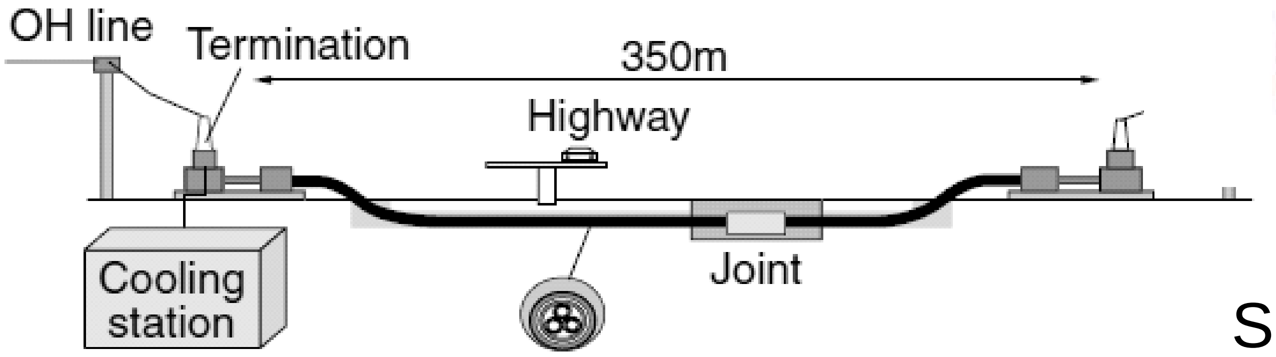


Fig. Outline of Albany HTS cable project

Sumitomo Electric Industries, 2007

HTS Cable (by Sumitomo Electric Industries)

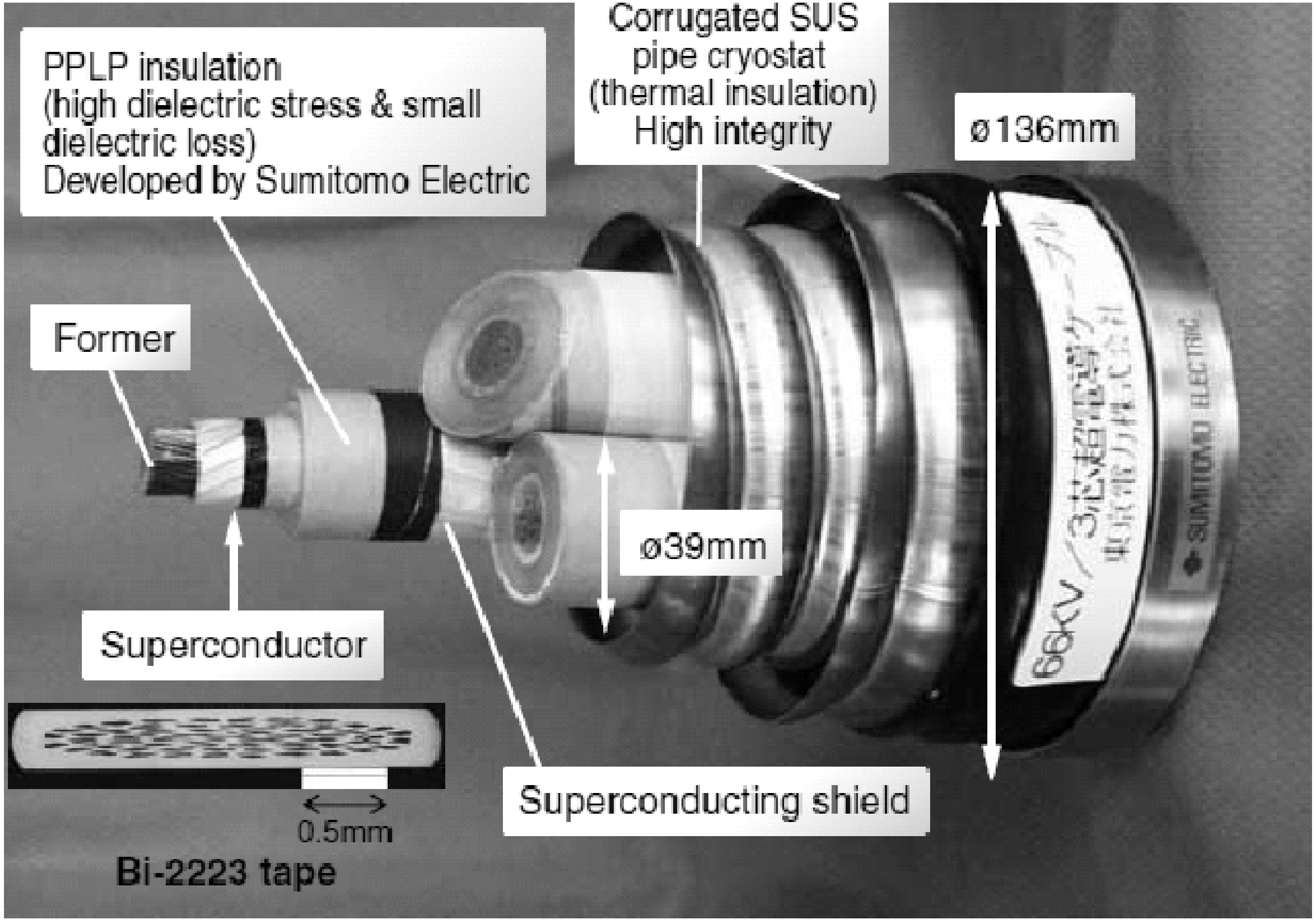


Fig. Three-cores-in-one-cryostat HTS cable (Cold dielectric, 100 m, 114 MVA, 1000 A)

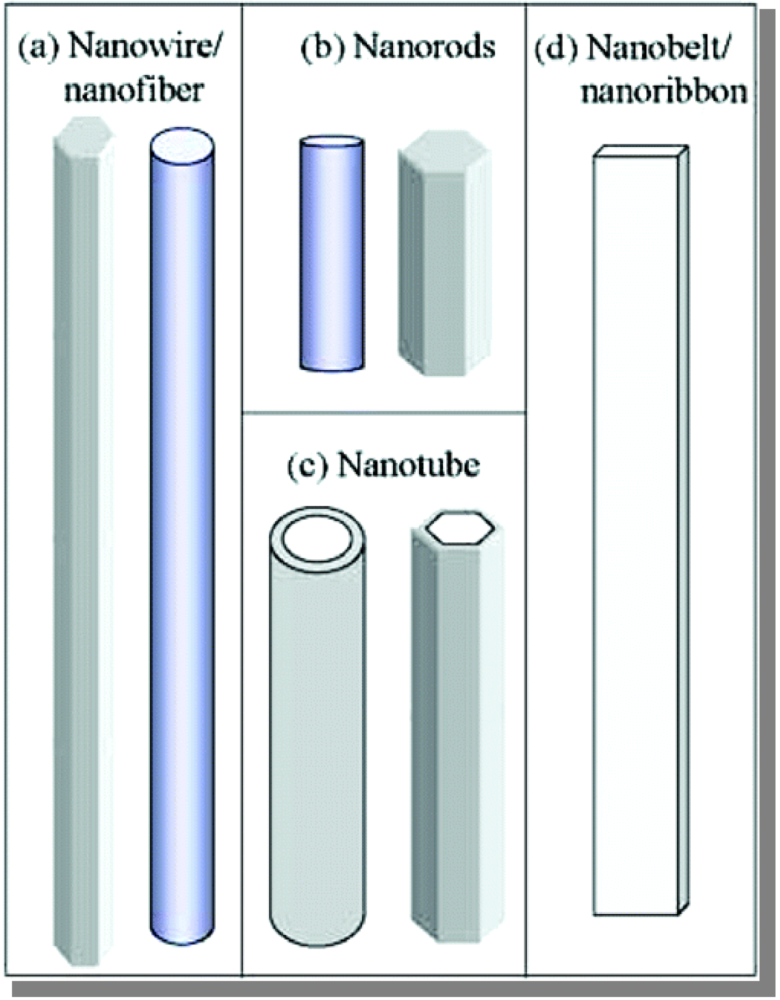
One-dimensional (1D) nanomaterials

- Materials with 1D morphology (diameter is < 100 nm)

- After the finding and application of carbon nanotubes, various inorganic and organic 1D nanomaterials are developed.

non-oxide: carbon, BN...
oxide: TiO_2, ZnO, V_2O_5
organic

1D nanomaterials: Classification / Merits and demerits



Y. Ding et al., J. Phys. Chem. B, **108**, 12280, 2004

Hollow shape:
  nanotube

Solid shape:
  nanorod   relatively small aspect ratio
  nanowire   short fiber / fine fiber
  nanofiber   long fiber (large aspect ratio)
  nanoribbon, nanobelt etc.

High surface area

High crystallinity (not always)
  (less defect)

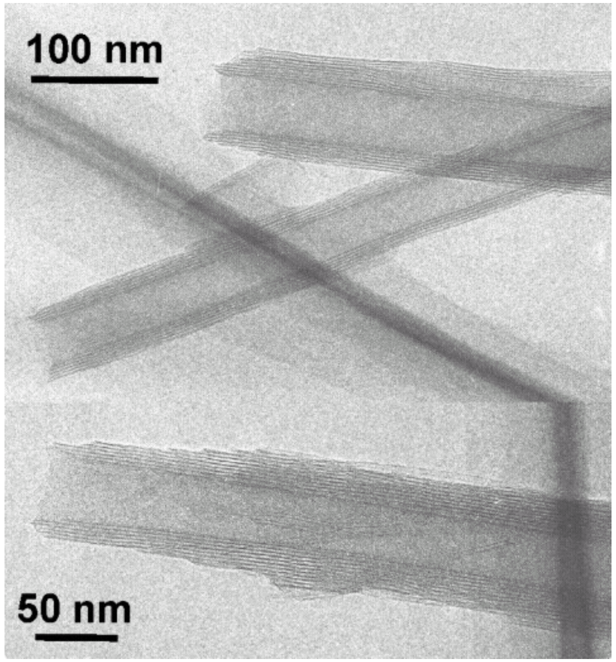
Unique properties
  - Electrical properties
  - Magnetic properties
  - Storage

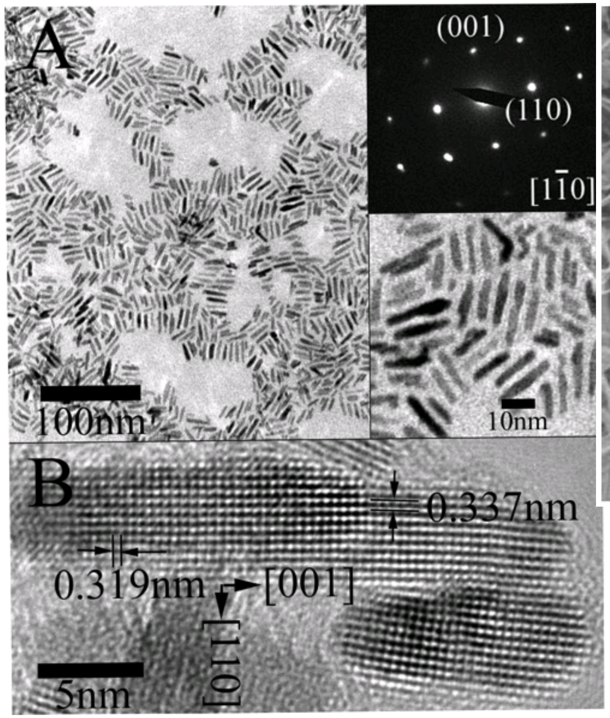
Some examples of 1D nanomaterials

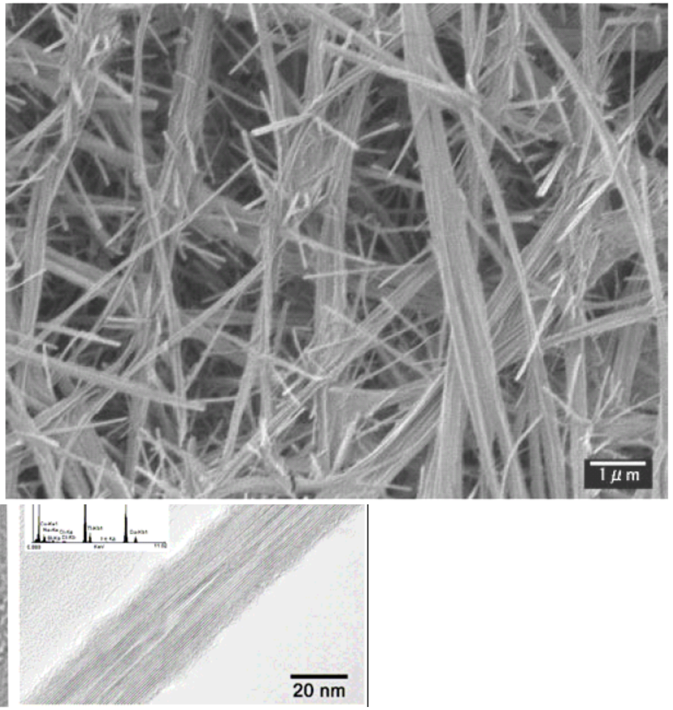
Nanotubes

Nanorods

Nanofibers







Vanadium Oxide Nanotubes
Outer Diameters : 15-100 nm
Inner Diameters : 5-50 nm
Length : 0.5-15 μm

H.-J. Muhr et al., Adv. Mater. 2000, 12, 231

Tin Oxide Nanorods
Diameter : 2.5-5 nm
Length : 15-20 nm

B. Cheng et al., J. Am. Chem. Soc., 2004, 126 (19), 5972.

Titanate Nanofibers
Diameters : 20-50 nm
Length : 10 μm – 500 μm

Y. Suzuki, S. Pavasupree, S. Yoshikawa, and R. Kawahata, J. Mater. Res., 20 (2005) 1063-1070.

TiO_2 and TiO_2-related titanate

TiO_2 a wide gap semiconductor

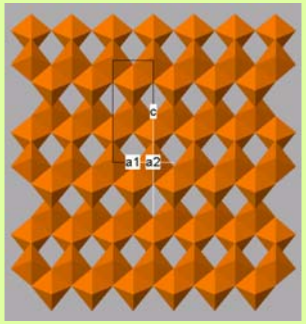
(mainly three polymorphs and some rare polymorphs)

rutile

Thermodynamically stable
Paint, pigment, chemicals

anatase

photocatalyst
solar cells



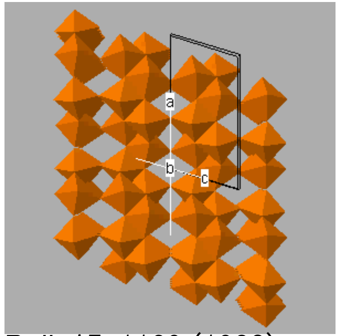
brookite

photocatalyst
(for visible light)
Rather difficult to synthesize

TiO_2 (B) (monoclinic)

4th mineral TiO_2
"TiO_2 bronze"

energy storage



R. Marchand, *Mat. Res. Bull.*, **15**, 1129 (1980).

TiO_2 and TiO_2-related titanate

TiO_2-related titanate

Titanate framework + cation
ex. $Na_2Ti_3O_7$, $K_2Ti_4O_9$, $H_2Ti_3O_7$,...

Layered titanate ($A_2Ti_nO_{2n+1}$), A cite can be ion-exchangeable

Tunnel structured titanate (e.g. $A_2Ti_6O_{13}$) can be also ion-exchangeable

Anisotropyic crystal growth (1D or 2D)

Hydrogen titanates (with adsorbed or crystalline H_2O) transform to TiO_2 by heating
--> precursor of TiO_2 nanowire and nanotubes

TiO_2-derived 1-D nanomaterials

TiO_2 powders

- Pigments, cosmetics
- Dielectric materials
- Photocatalyst
- Dye-sensitized solar Cell (DSC)

etc.

Raw Material Production in Japan

Al_2O_3: 28.7 billion yen (2003, estimated)

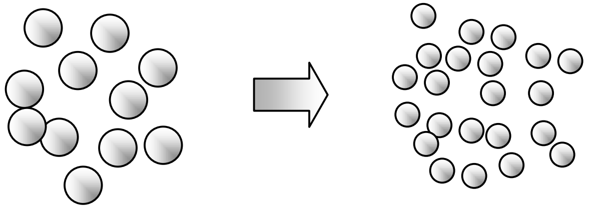
$BaTiO_3$: 20.5 billion yen (2003, estimated)

TiO_2: 11.8 billion yen (2003, estimated)

JFCA report for Ceramic Industry

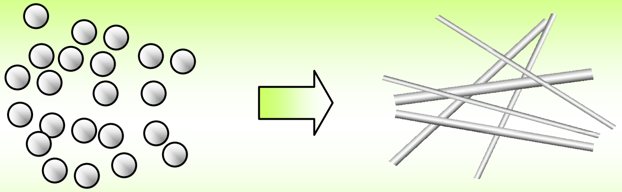
Conventional Approach for High performance TiO_2 production

Improvement via powder refinement



New Approach for High performance TiO_2 production

Further Improvement using Morphological Control



e.g., Light scattering, Higher conductivity...

TiO_2-related nanotubes

Anodic Oxidation

- Anodic Porous Alumina Template
  P. Hoyer, *Langmuir*, **12**, 1411 (1996).; *Adv. Mater.*, **8**, 857 (1996).
- Direct Anodic Oxidation of Titanium
  D. Gong et al., *J. Mater. Res.*,**16**, 3331 (2001).
  O. K. Varghese et al., *J. Mater. Res.*, **18**, 156 (2003).; *Adv. Mater.*, **15**, 624 (2003).

Template

- Polymer template (poly (L-lactide))
  R. A. Caruso et al., *Adv. Mater.*, **13**, 1577 (2001).
- Organic crystal (ammonium tartrate)
  F. Miyaji et al., *J. Ceram. Soc. Jpn.*, **109**, 924 (2001).
- Inorganic crystal (Platinum salt)
  C. Hippe, et al., *Microporous Mesoporous Mater.*, **31**, 235 (1999).
- Carbon nanotubes
  J. Sun, et al., *J. Mater. Sci. Lett..*, **22**, 339 (2003).

Chemical Treatment

- Hydrothermal alkali treatment of TiO_2 powder
  T. Kasuga et al., *Langmuir*, **14**, 3160 (1998). ; *Adv. Mater.*, **11**, 1307 (1999).

Hydrothermal alkali treatment of TiO_2 powder（1）

Pioneer work by Kasuga et al. (Chubu Electric Power Co.), 1998

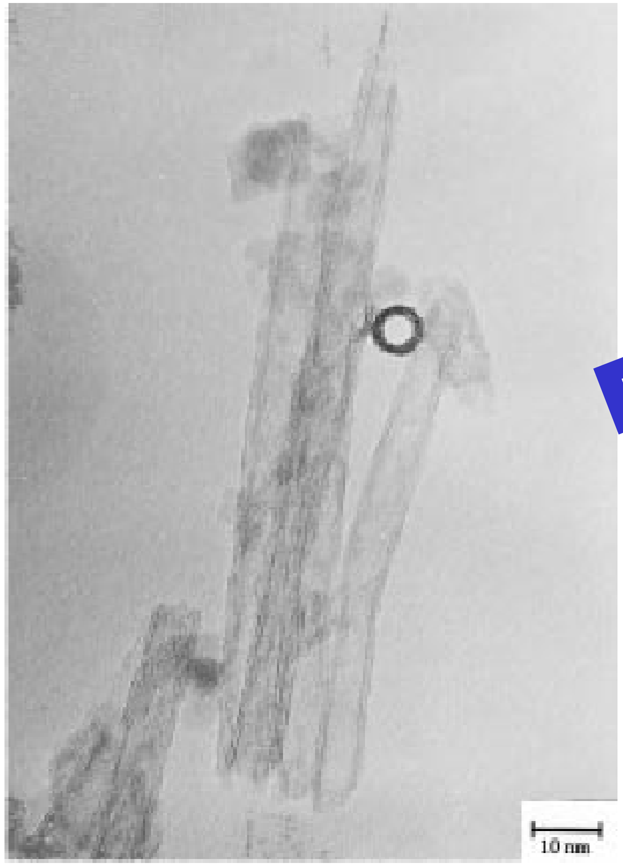


Figure 2. TEM photograph of $80TiO_2 \cdot 20SiO_2$ (in mol %) powders treated with 10 M NaOH aqueous solution for 20 h at 110 °C.

Langmuir, **14**, 3160 (1998).

Nanotube formation by hydrothermal treatment of TiO_2 powder in NaOH aq.

Epoch-making !

- Low cost, Mass productive
- Without template, Environmental friendly

Several groups follow/improve the processing since 2001.

G. H. Du et al., *Appl. Phys. Lett.*, **79**, 3702 (2001).
Q. Chen et al., *Acta Crystallogr. B*, **58**, 587 (2002).
Q. Chen et al., *Adv. Mater*., **14**, 1208 (2002).
X. Sun et al., *Chem. Eur. J*, **9**, 2229 (2003).
....

Hydrothermal alkali treatment of TiO_2 powder（2）

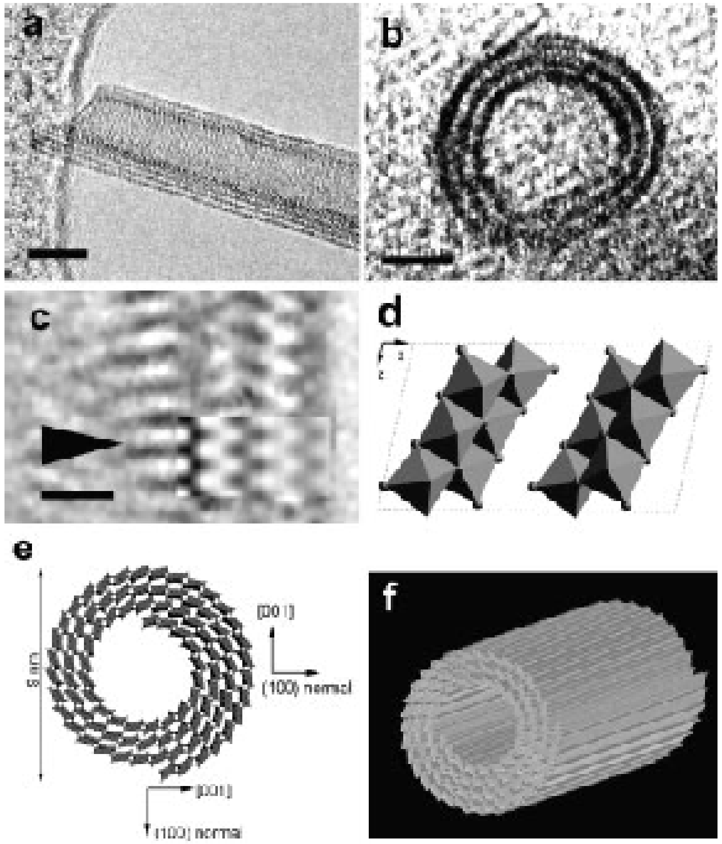


Fig. 3. Nanotube structure. a) HRTEM image showing a nanotube with open end and three layers at the top but four layers at the bottom. Scale bar: 6 nm. b) HRTEM image of the cross section of a nanotube showing its scroll character. Scale bar: 3 nm. c) Enlarged HRTEM image of a part in (a) pasted with a simulated image (pointed) using the present structure model. The agreement between experimental and simulated images is excellent. Scale bar: 1 nm. d) Structure model of one unit cell of $H_2Ti_3O_7$ on the [010] projection. e) Schematic drawing of the structure of the present nanotube. The crystal orientations indicated are the orientations according to the $H_2Ti_3O_7$ layer. f) Three-dimensional drawing of a nanotube.

Adv. Mater., **14**, 1208 (2002).

Du, Chen et al.:

- Proposing “Scroll mechanism” via thorough TEM analysis
- $H_2Ti_3O_7$ (layered titanate) rather than TiO_2

G. H. Du et al., *Appl. Phys. Lett.*, **79**, 3702 (2001).
Q. Chen et al., *Acta Crystallogr. B*, **58**, 587 (2002).
Q. Chen et al., *Adv. Mater.*, **14**, 1208 (2002).

X. Sun et al.:

$Na_2Ti_3O_7 \rightarrow Na_xH_{2-x}Ti_3O_7$

Ion-exchange mechanism

X. Sun, *Chem. Eur. J*, **9**, 2229 (2003).

Porous materials: increasing demand

- Recently, porous materials have attract much attention for the energy/environment applications.

- There are so many variations of microstructure, processing, and evaluation methods.

- In the lecture,
  - Classification of porous materials (especially inorganic)
  - Processing methods
  - Evaluation methods
  - Examples of Development

  will be introduced.

- Then, let's think about "which materials will be *hot* in future".

Definition of porous materials ?

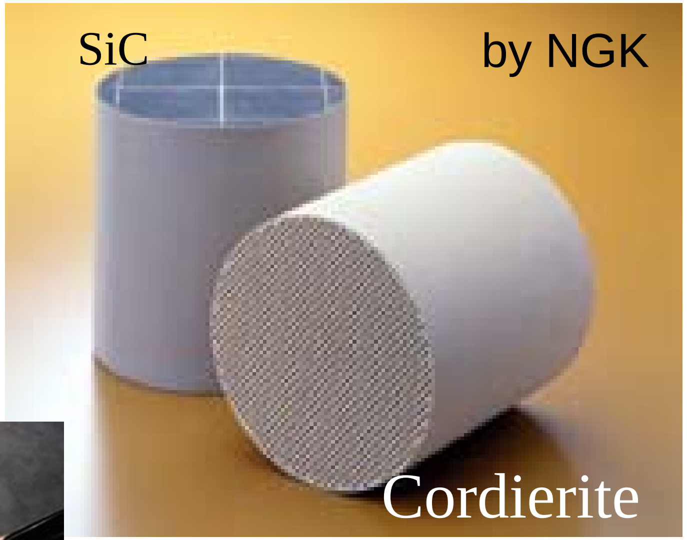
- There is no clear definition by the porosity

  ~~(i.e. > xx vol%, we can say they are porous materials)~~
- However, in some applications, "> 10 vol% porosity" signifies it is porous.   (i.e., depending to the applications)

For some ordinary porous materials
  Cordierite honeycomb : porosity of ~ 40 vol%

  Alumina (Al_2O_3) brick : porosity of ~ 75 vol%

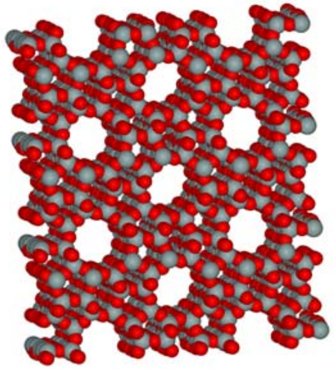
  Sponge-like porous SiC : porosity of ~ 85 vol%



Yoshihisa Beppu, Materials Integration, Vol.**15** [1], p17, 2002

Classification by the open pore-size diameter

Classification by IUPAC (International Union of Pure and Applied Chemistry)



ZSM-5 (wikipedia)

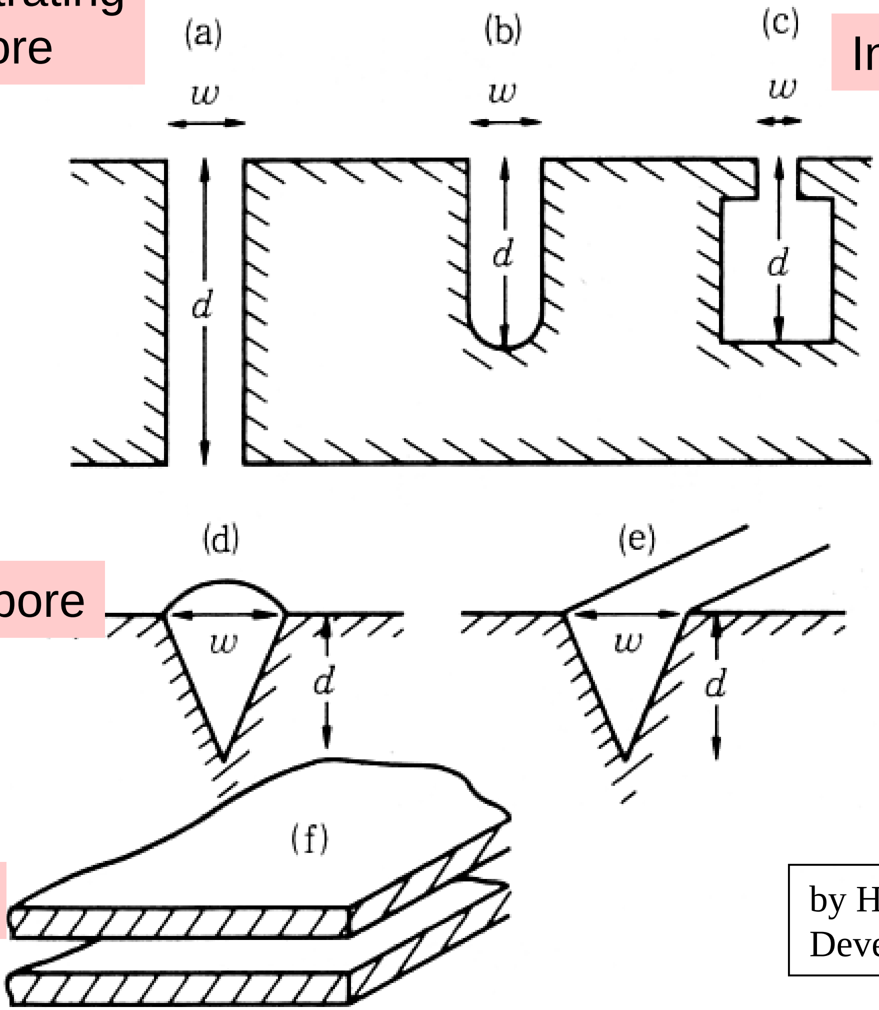
Micropore: < 2 nm
e.g., zeolite (vacancy within crystal structure)

Mesopore: 2-50 nm
e.g., silica gel, activated carbon

Macropore: > 50 nm
e.g., sintered porous filter, catalyst, catalyst support...

Recently, open pore of < 100 nm also called as "nanopore",
(but this is not an authorized technical term at this moment.

Morphology of open pores



penetrating pore

non-penetrating pore

Ink-bottle pore

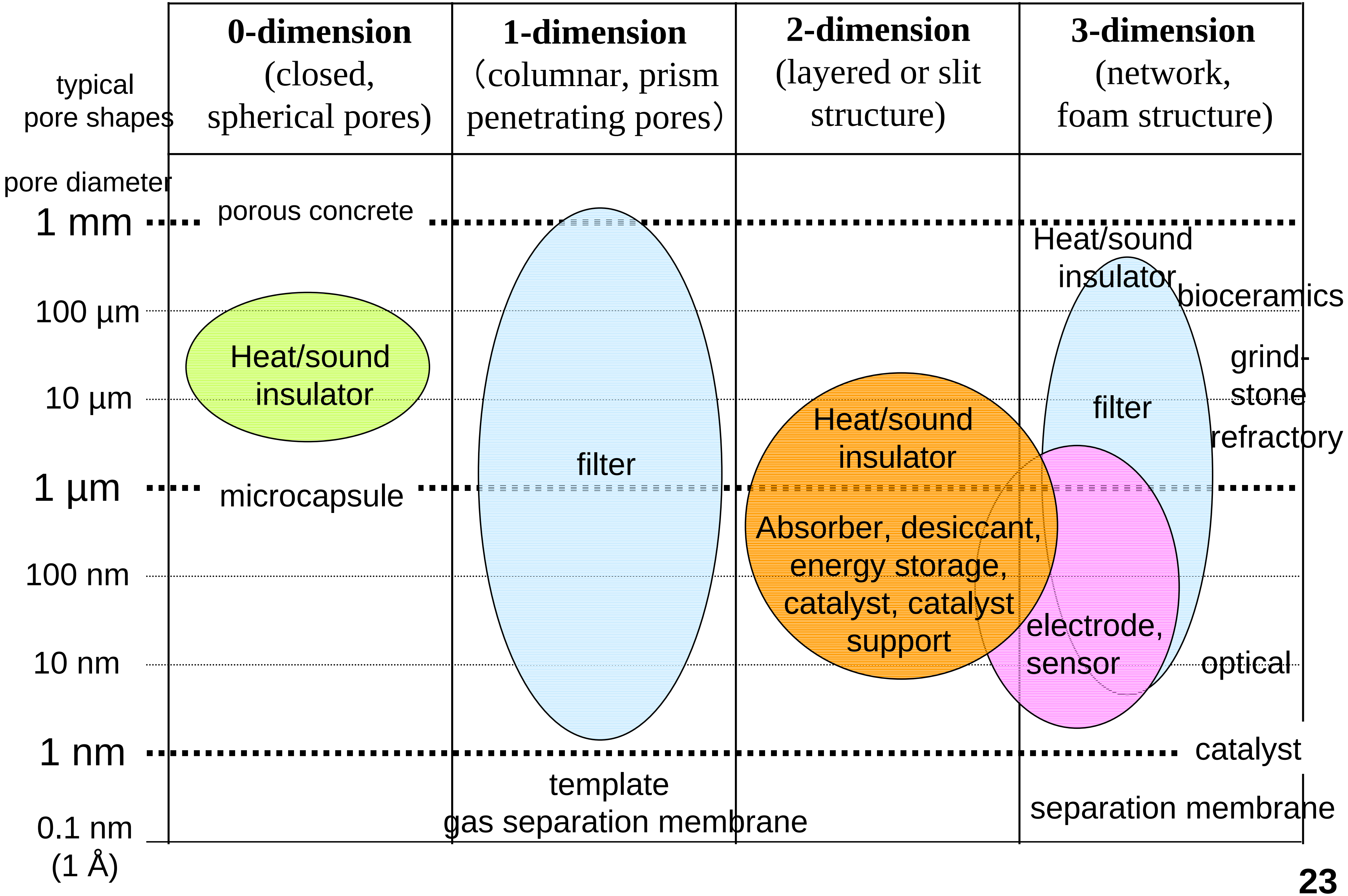
conical pore

wedge-shaped pore

Slit-shaped pore

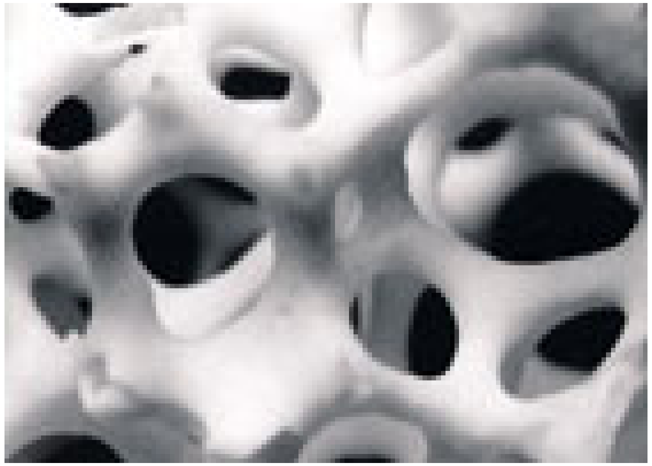
by Hattori & Yamanaka,
Development of porous ceramics

Porous materials map 1: Materials and applications

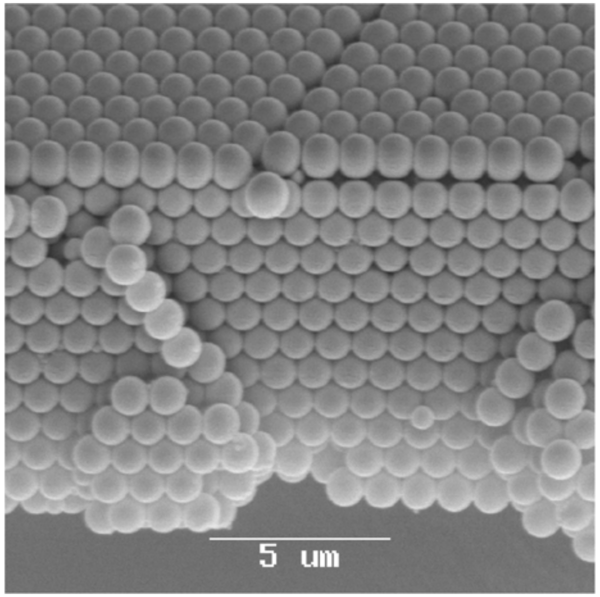


Some examples

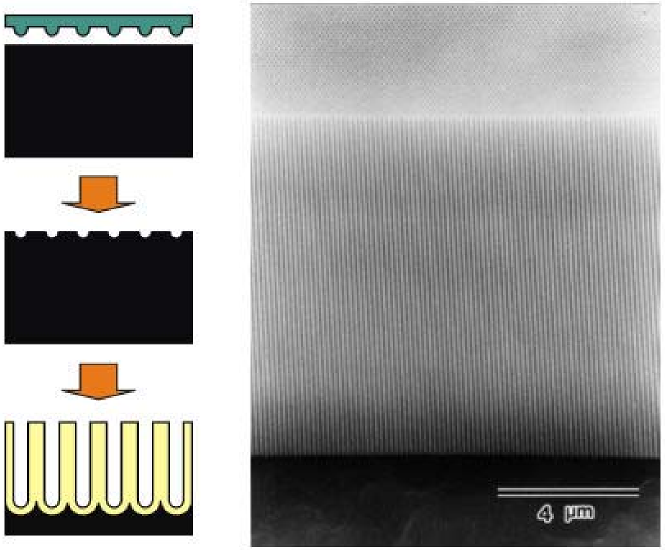
glass fiber thermal insulator (www.ipros.jp)



Ceramic form (by Bridgestone)



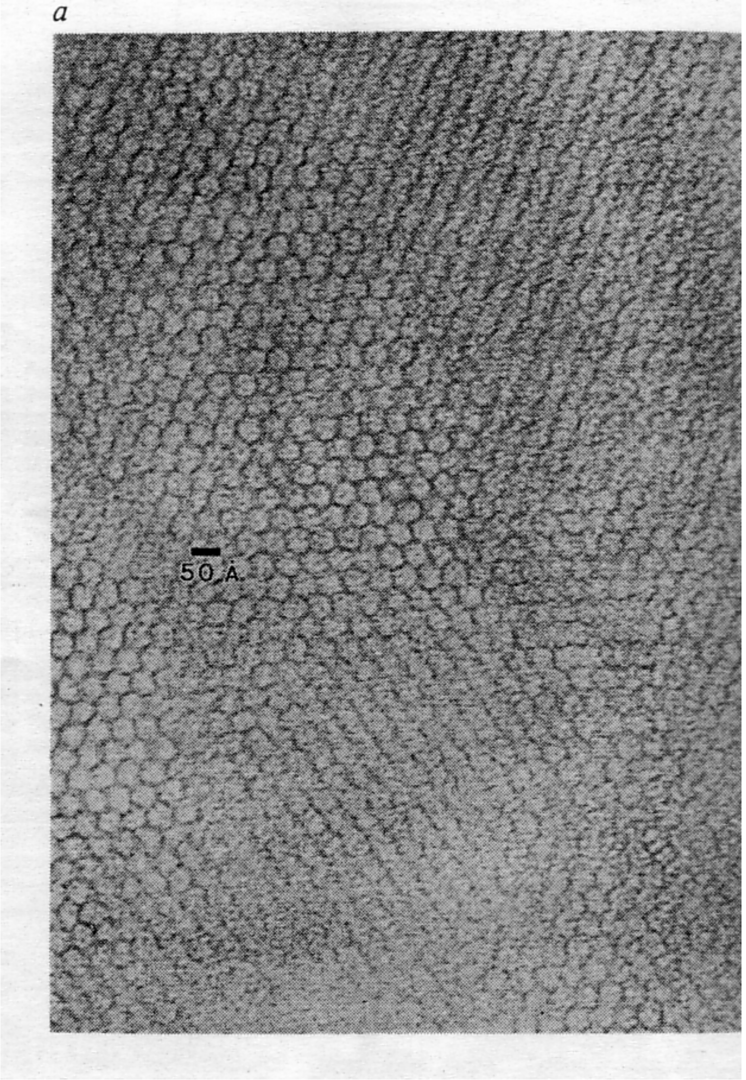
self-assembly opal structure (Thorsten Schweizer et al.)



Porous alumina by nano-imprinting
(by Prof. Hideki Masuda et al.)

One dimensional mesoporous material

MCM-41 (Mobile)



Bottom-up self assembly

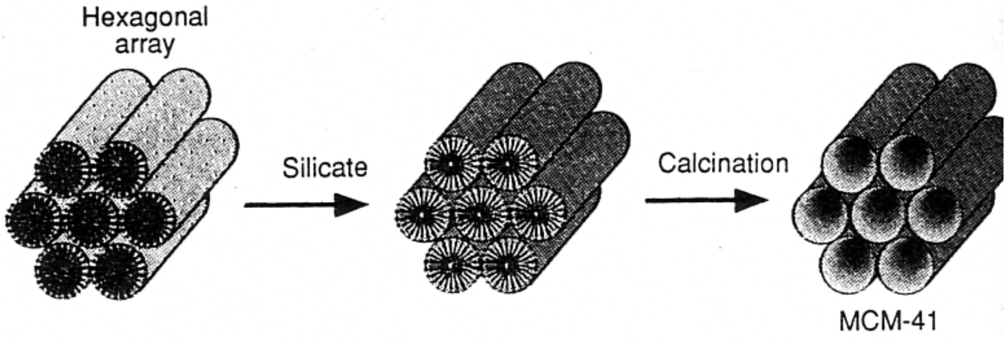
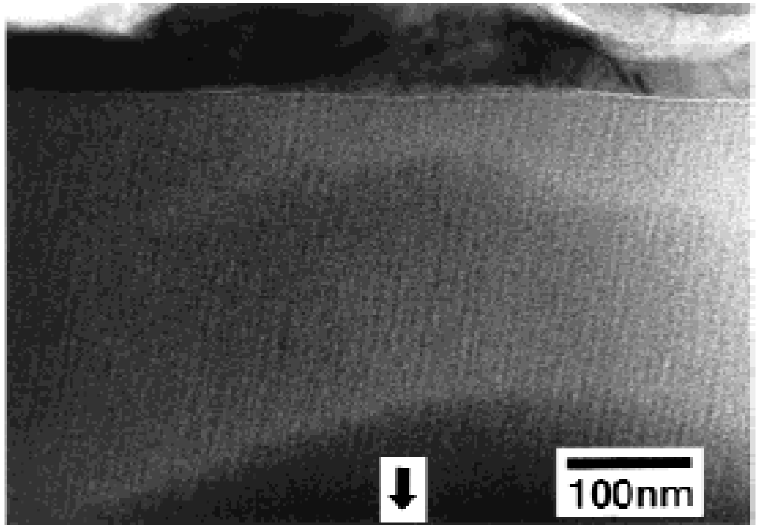


FIG. 5 Schematic drawing of the liquid-crystal templating mechanism. Hexagonal arrays of cylindrical micelles form (possibly mediated by the presence of silicate ions), with the polar groups of the surfactants (light grey) to the outside. Silicate species (dark grey) then occupy the spaces between the cylinders. The final calcination step burns off the original organic material, leaving hollow cylinders of inorganic material.

C. T. Cresge et al., *Nature*, **359**, 710 (1992)

Unidirectional mesoporous film by phase separation



Using eutectic decomposition method

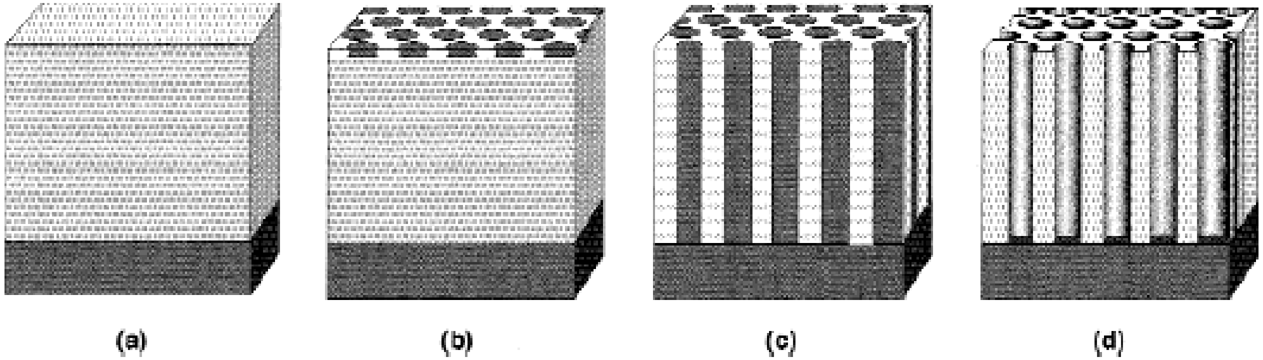
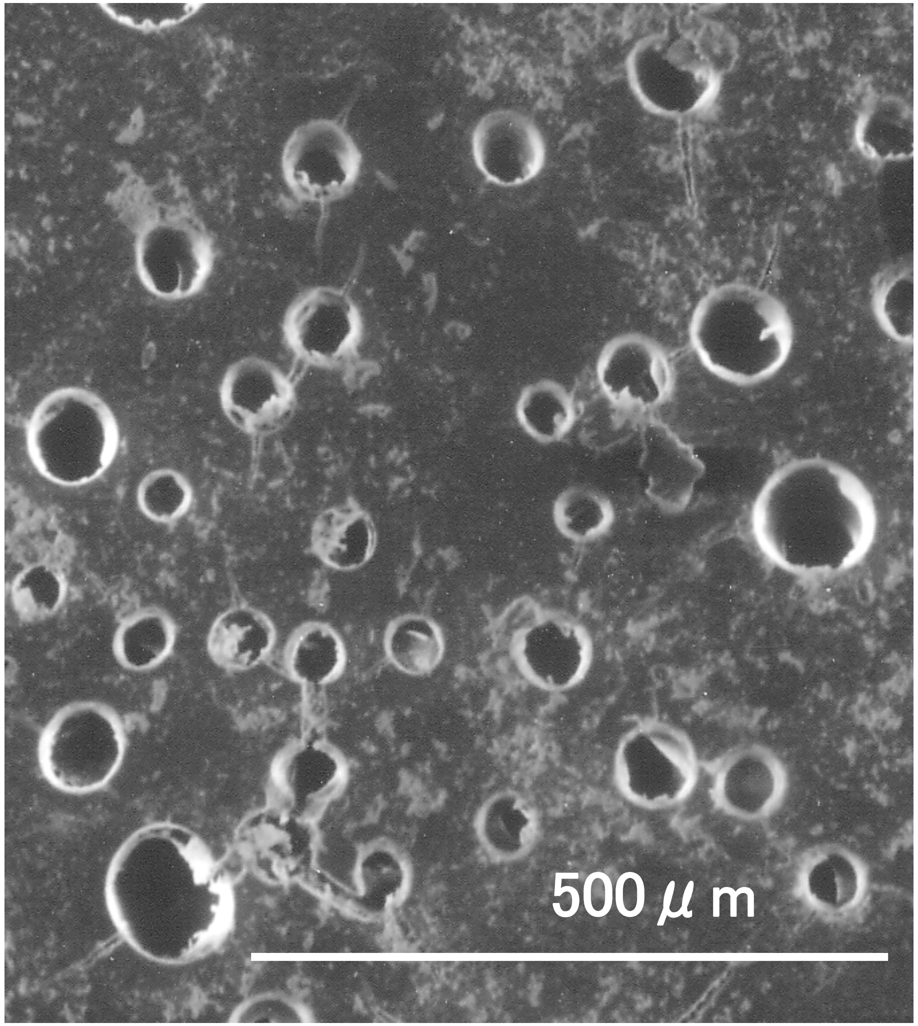


Fig. 1. Schematic drawings of the fabrication process of the eutectic microstructure and one-dimensional through channels: (a) deposition of amorphous film on substrate, (b) nucleation of eutectic microstructure on the film surface, (c) growth of one-dimensional eutectic structure and completion of the eutectic reaction, and (d) leaching out of precipitated needlelike iron oxide crystals by selective etching.

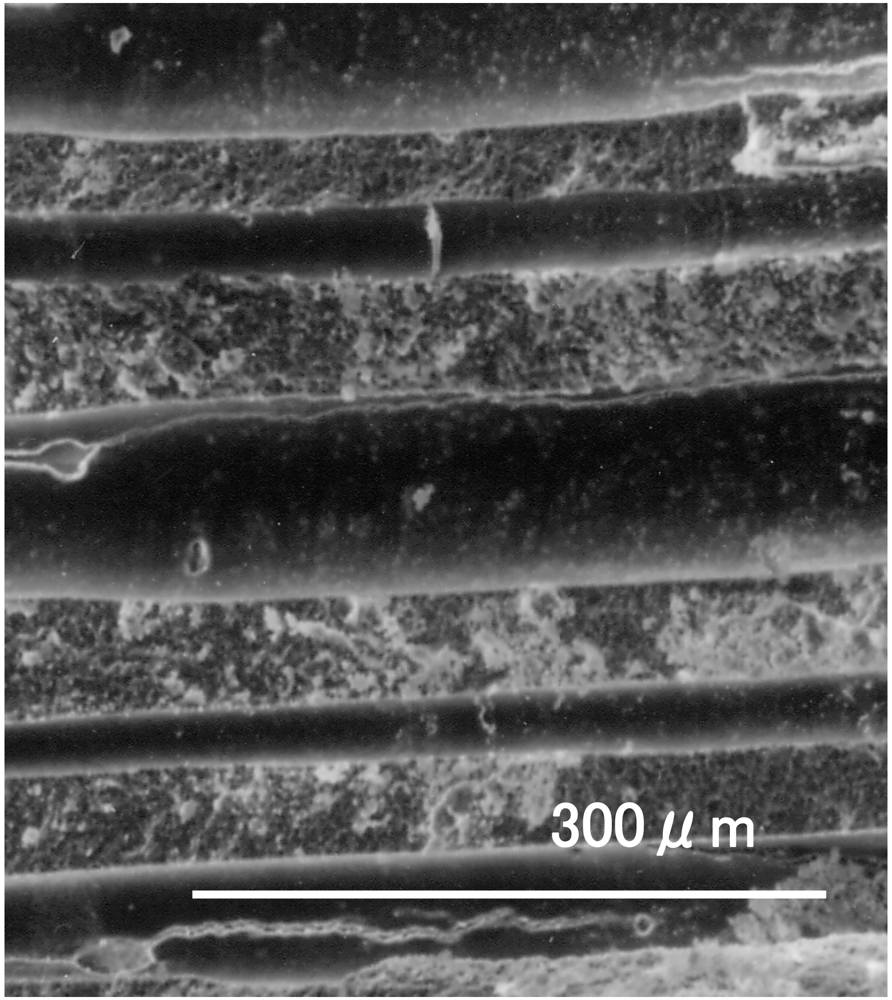
S. Kondo et al., *J. Am. Ceram. Soc.*, **82** [1] 209 (1999).

Macroporous Al_2O_3 by Electrophoretic Deposition (EPD) method

Top



cross section



by Prof. Nakahira at Osaka Prefecture Univ.

Unidirectional solidification and Selective leaching

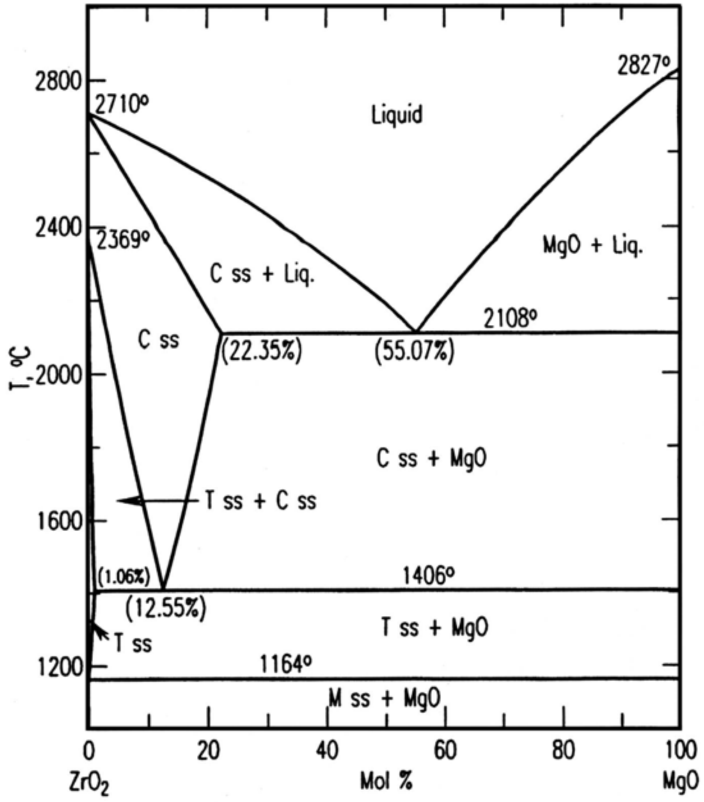
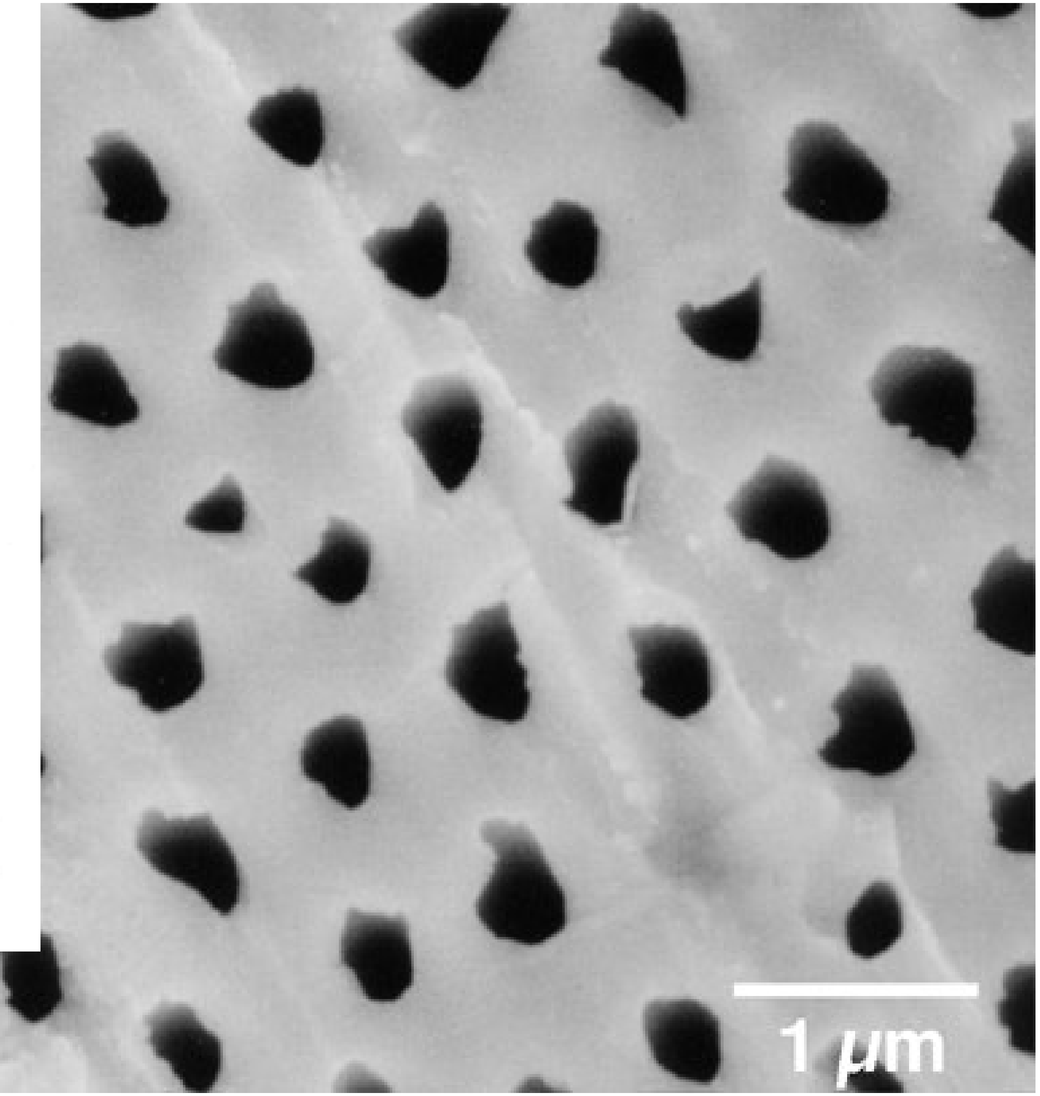


Fig. **Zr-073**—System ZrO_2-MgO (optimized). C ss = solid solution based on cubic ZrO_2; T ss = solid solution based on tetragonal ZrO_2; M = monoclinic ZrO_2.

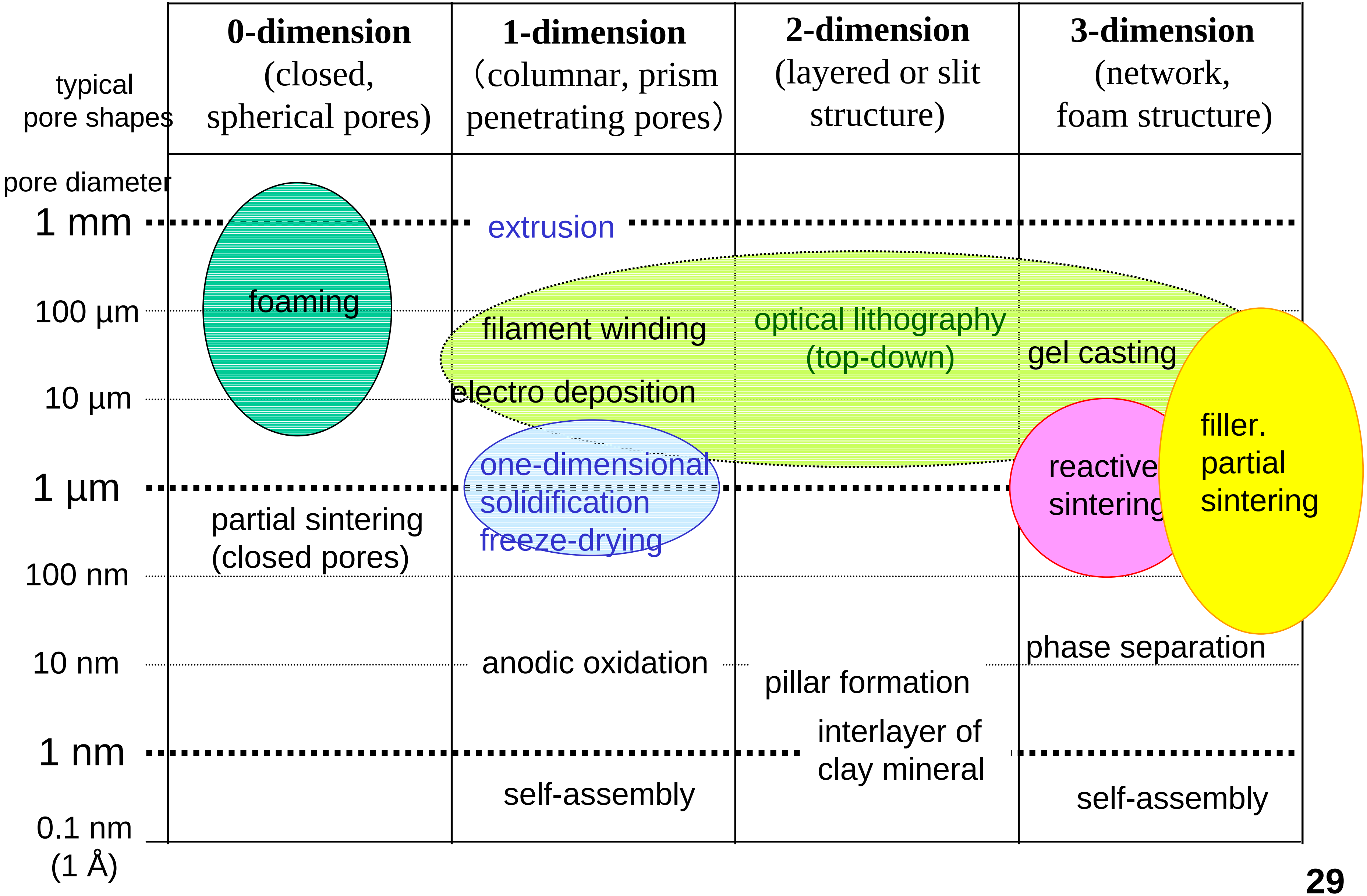
Y. Du and Z. P. Jin, *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, **15** [1] 59-68 (1991).

Porous ZrO_2

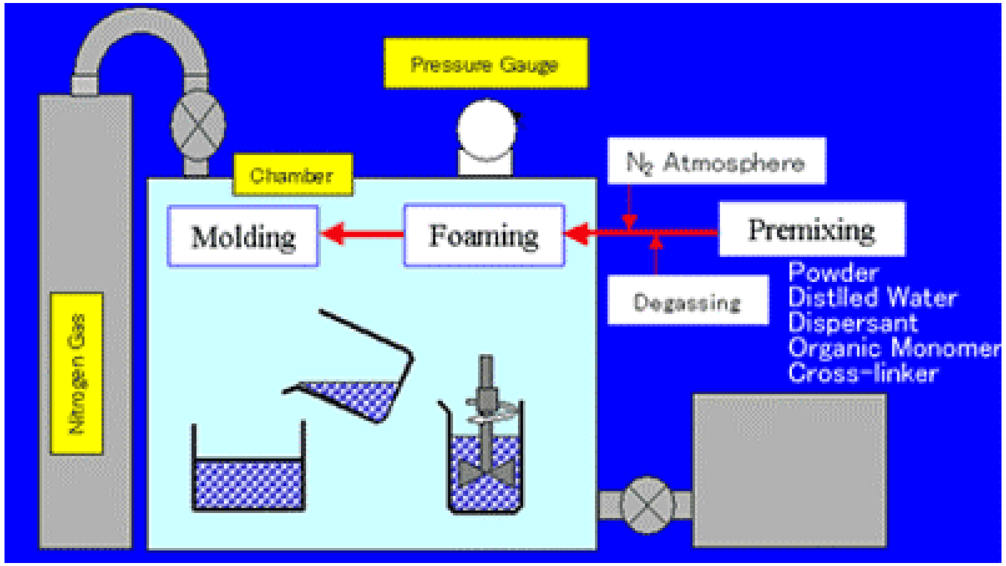


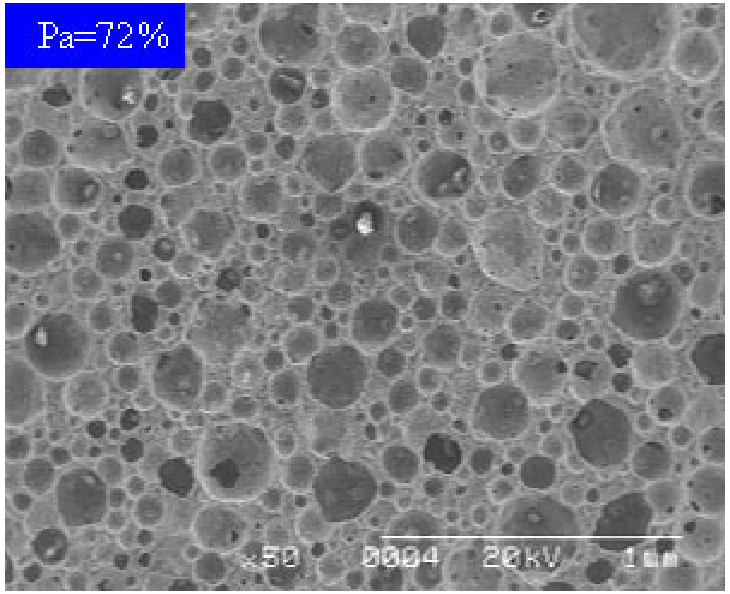
Y. Suzuki et al., *Ceram. Eng. Sci. Proc.*, **21** [4] 19-24 (2000).

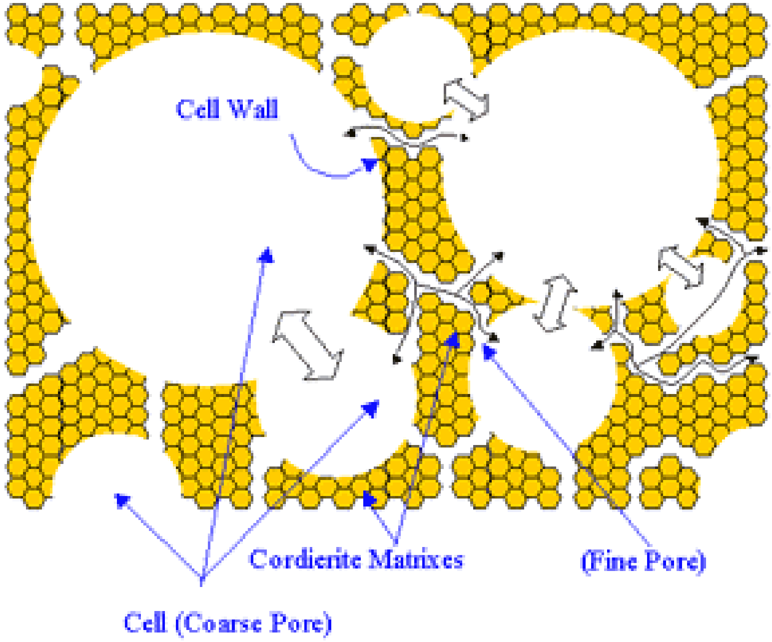
Porous materials map 2: Processes of porous materials

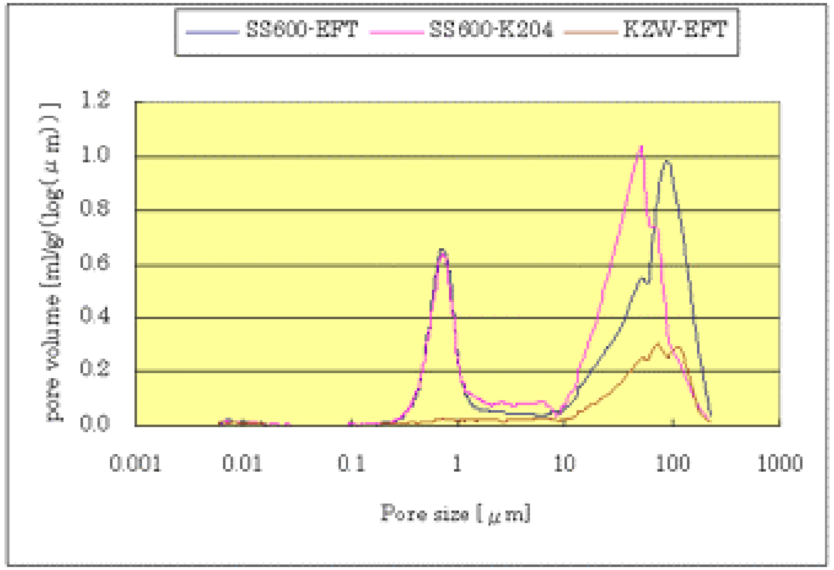


Using bubbles









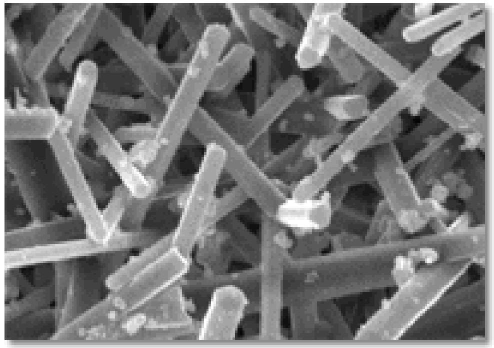
Narita Seitosho, http://www.naritaseitosho.co.jp/

Partial sintering of anisotropic particles

"Poreceram" module

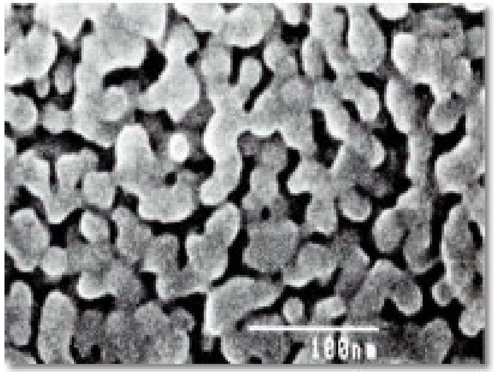
Using the anisotropic crystal growth of Si_3N_4, low pressure-loss porous materials was developed (by Sumitomo Electric Industries Co.)

Pore Ceram (Porous Si_3N_4)

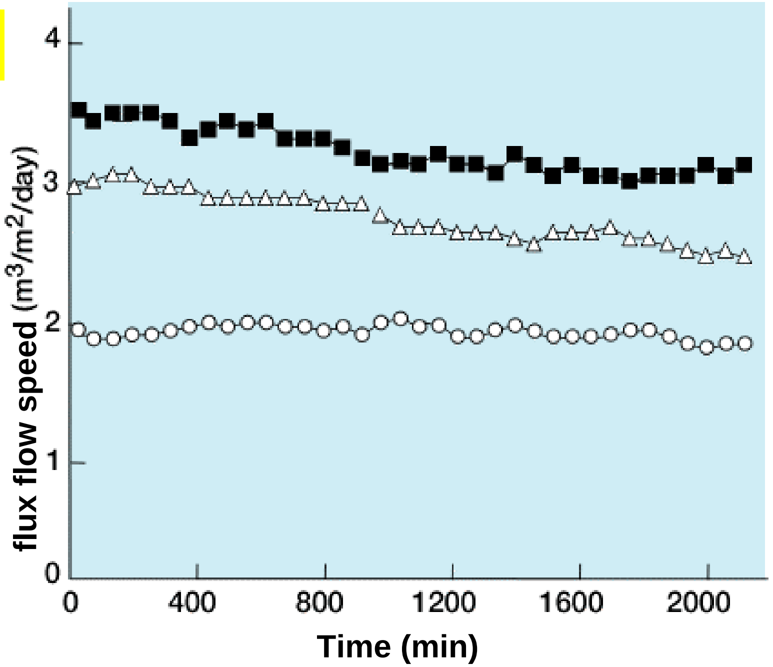


1 µm

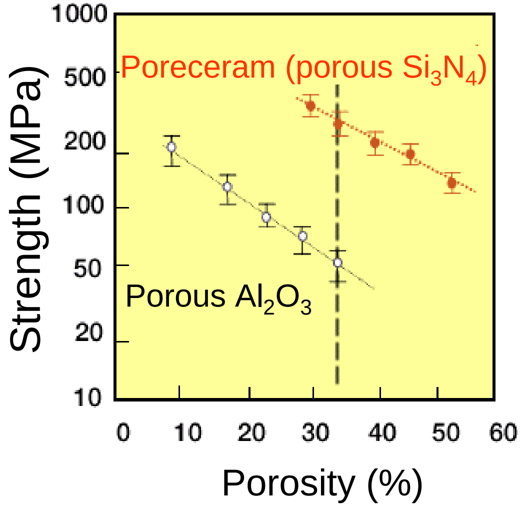
Porous Al_2O_3



0.1µm



Filter size: 0.05 µm
Slurry concentration: 9000 ppm
Differential pressure: 0.1 MPa
Time: 35 h



http://www.sei-sfp.co.jp/product/module/poreceram.html

Porous Si_3N_4 by Partial (confined) hot-pressing

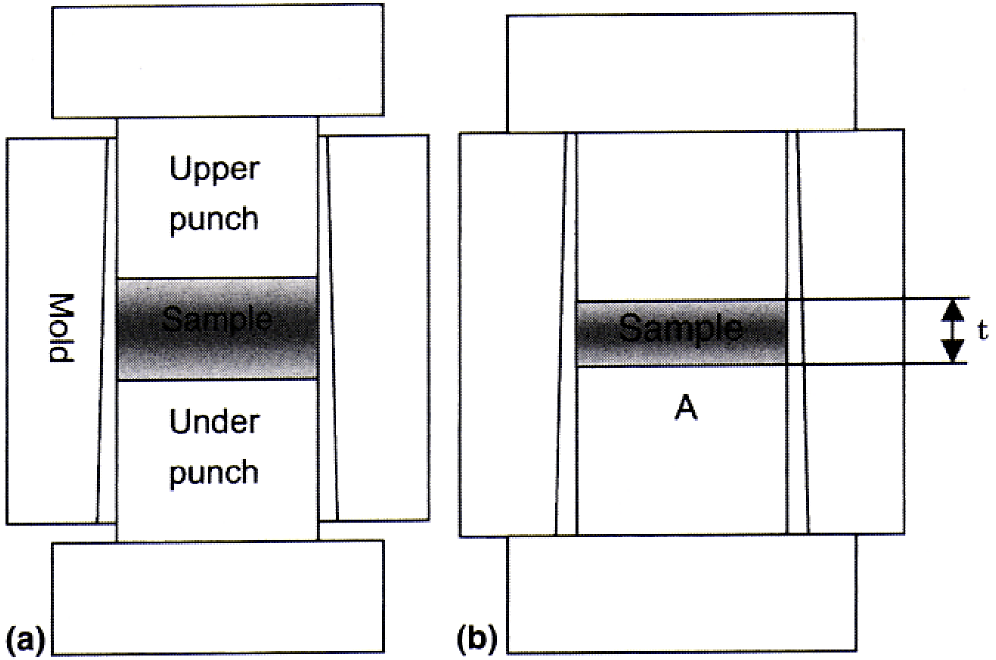


FIG. 1. Schematic diagram of the hot-pressing mold used for sintering.

J. F. Yang et al., *J. Mater. Res.*, **16** [7] 1915 (2001).

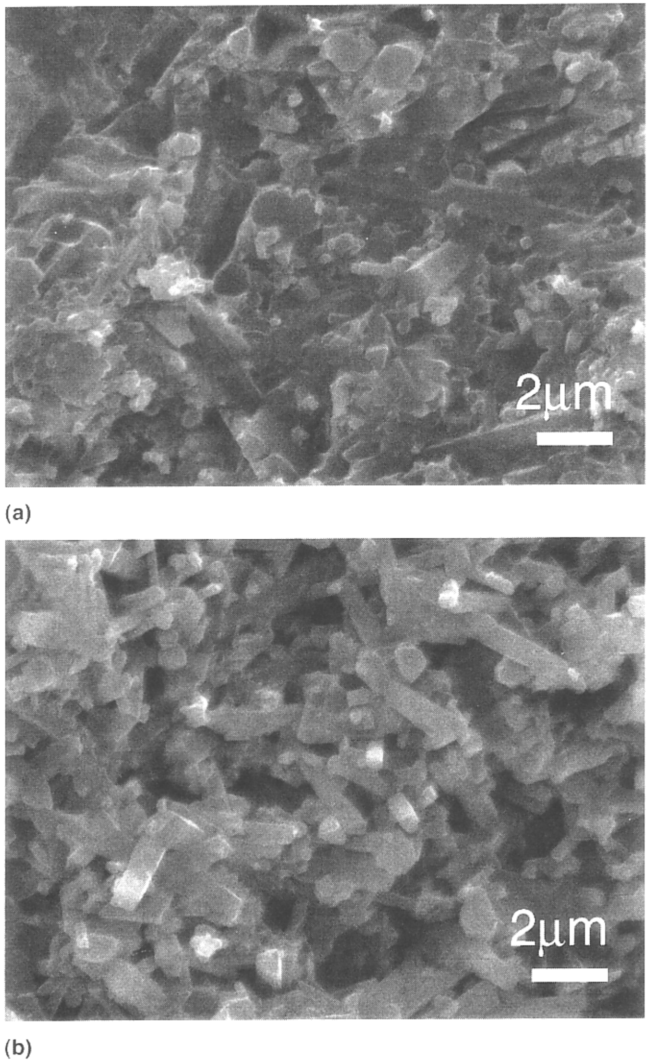
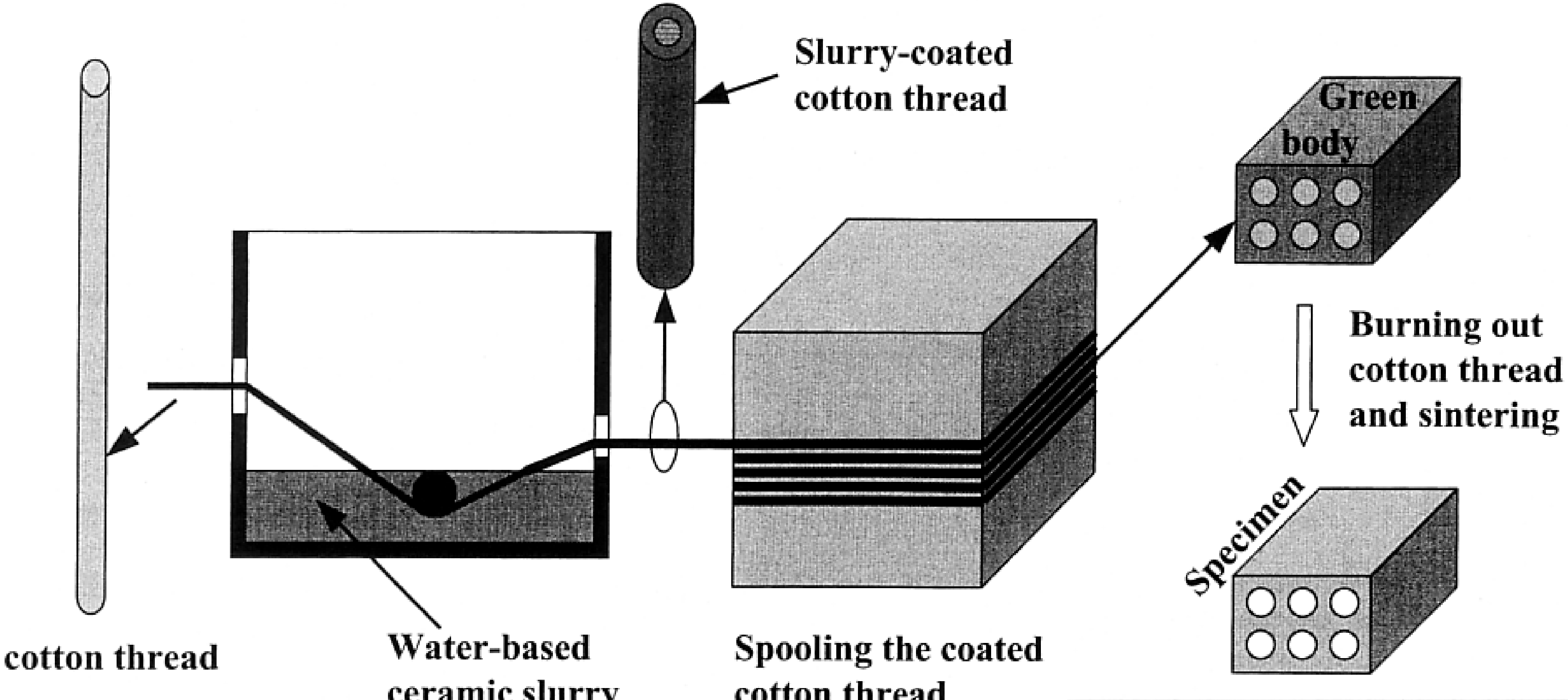
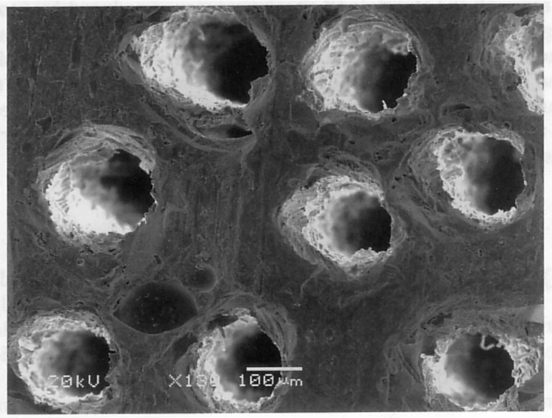


FIG. 3. Porous Si_3N_4 ceramic microstructure made by the PHP method. The porosities were (a) 0.004 and (b) 0.233.

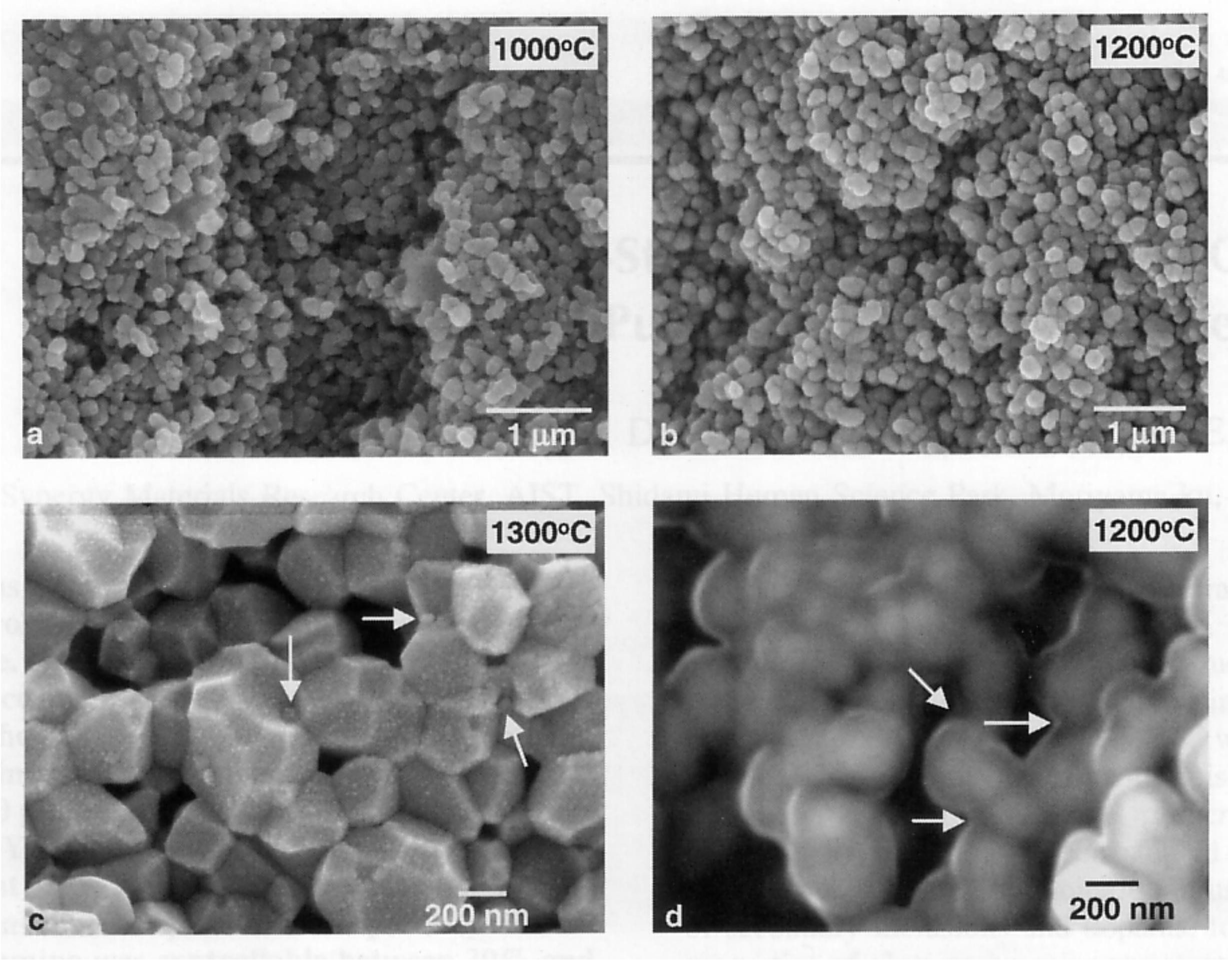
Filament winding (Unidirectional porous Al_2O_3)





G. J. Zhang et al., *J. Am. Ceram. Soc.*, **84** [6] 1395 (2001).

Pulse-electric current sintering (PECS) method



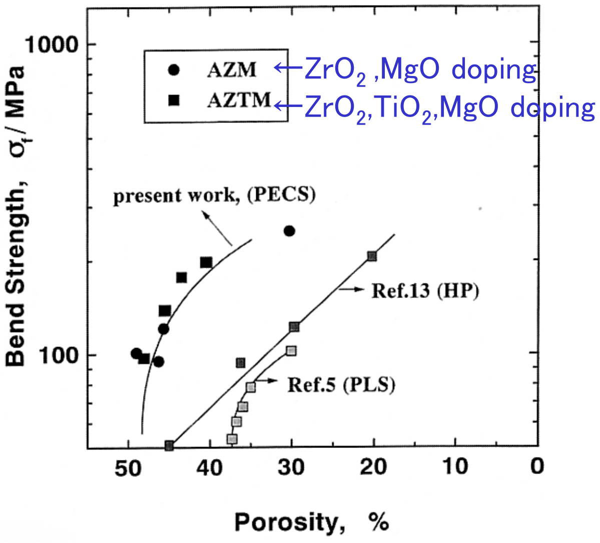
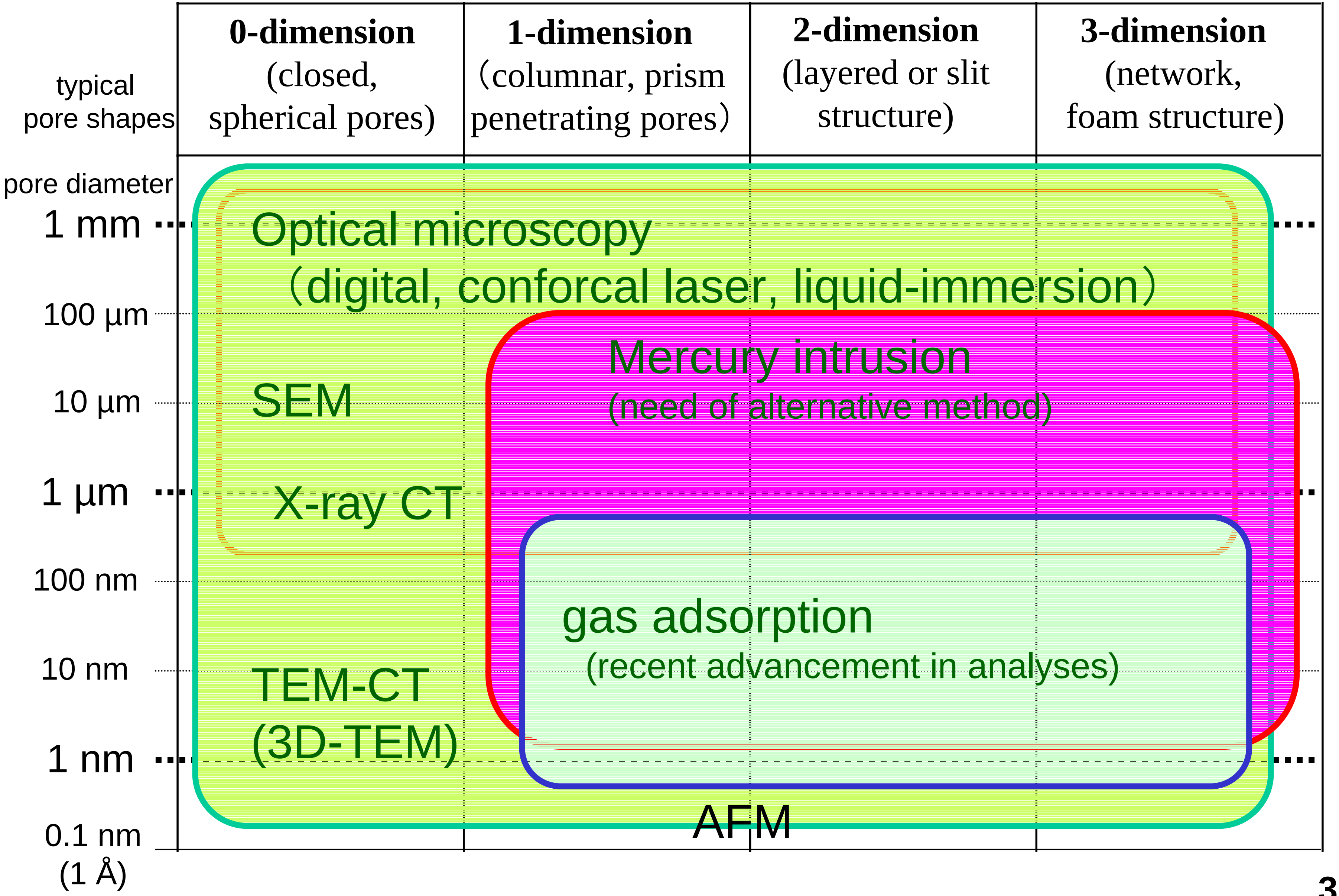


Fig. 2. Effect of porosity on flexural strength of alumina.

High strength Al_2O_3/3 vol% ZrO_2 porous material

D. Doni Jayaseelan et al.、*J. Am. Ceram. Soc.*, **85**, 267 (2002)

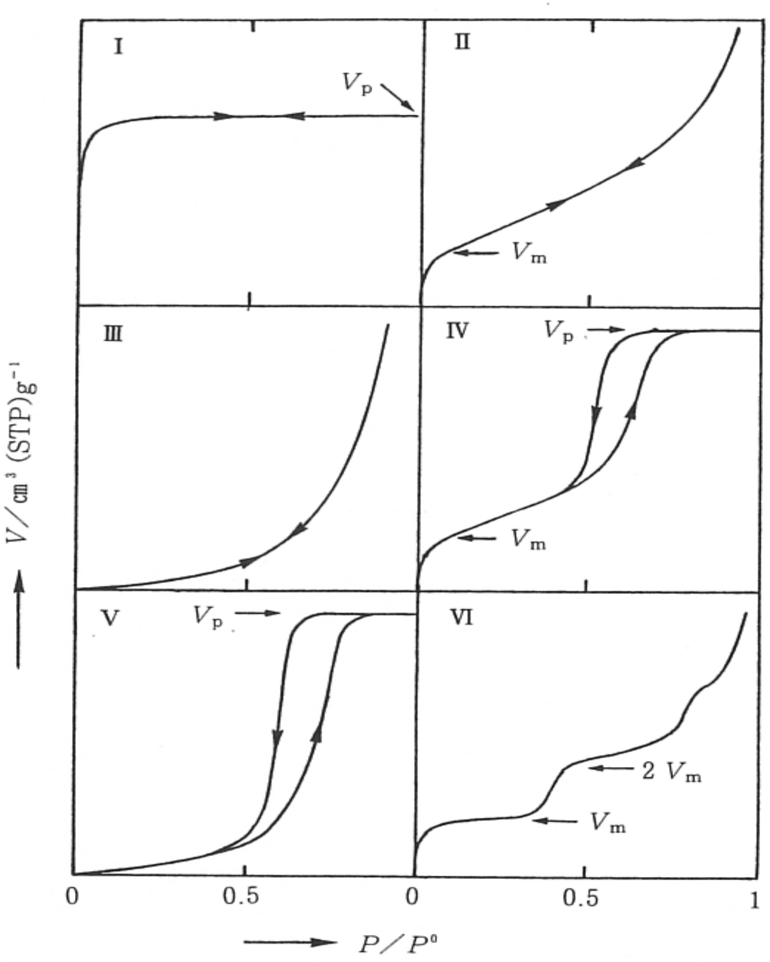
Porous materials map 3: Analyses methods



In addition, SAXS, gas-permeation etc.

Gas adsorption method (for BET, BJH methods etc.)

Quantachrome, Autosorb3



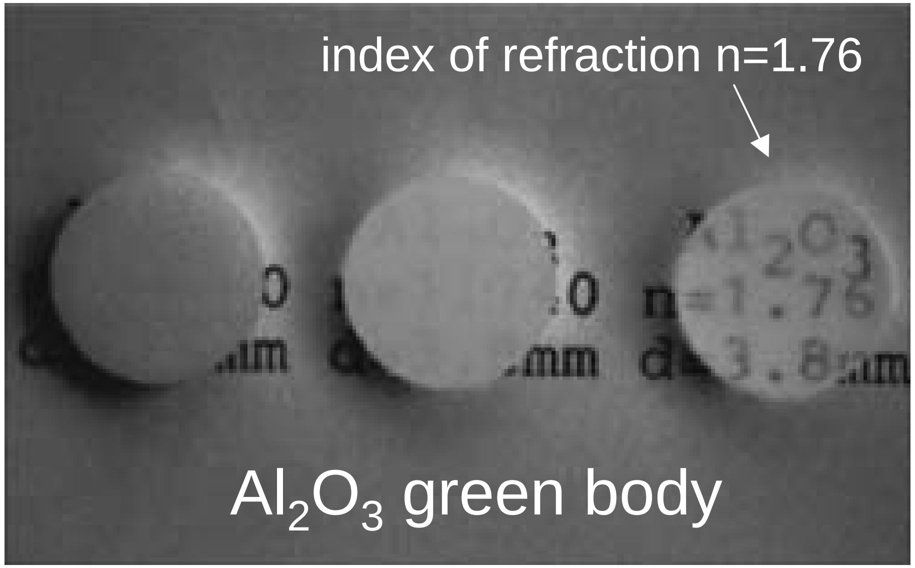
Recently, analytical method has been progressed rapidly. (combining molecular simulations)

Mercury intrusion method

- Versatile method for various open pore size (several nm - several 100 μm)
- Alternative method is required.

Quantachrome Pore Master GT

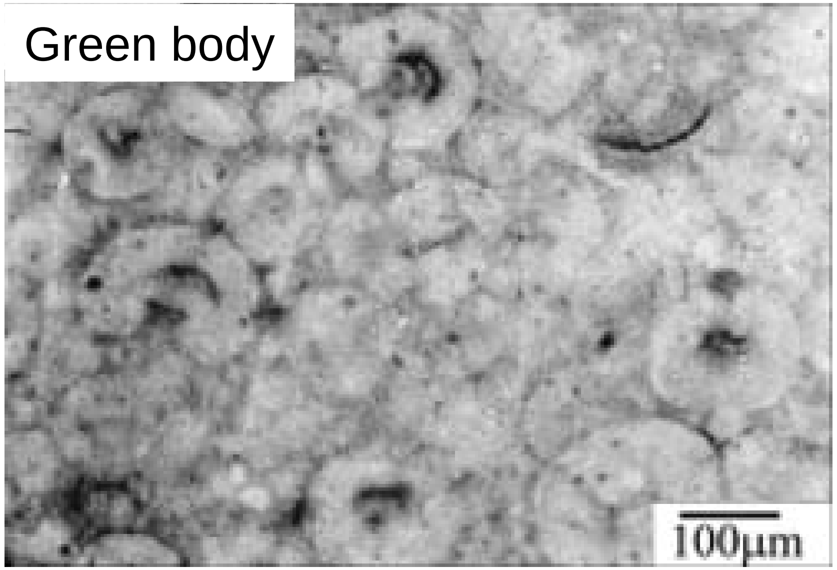
Liquid immersion method


index of refraction n=1.76

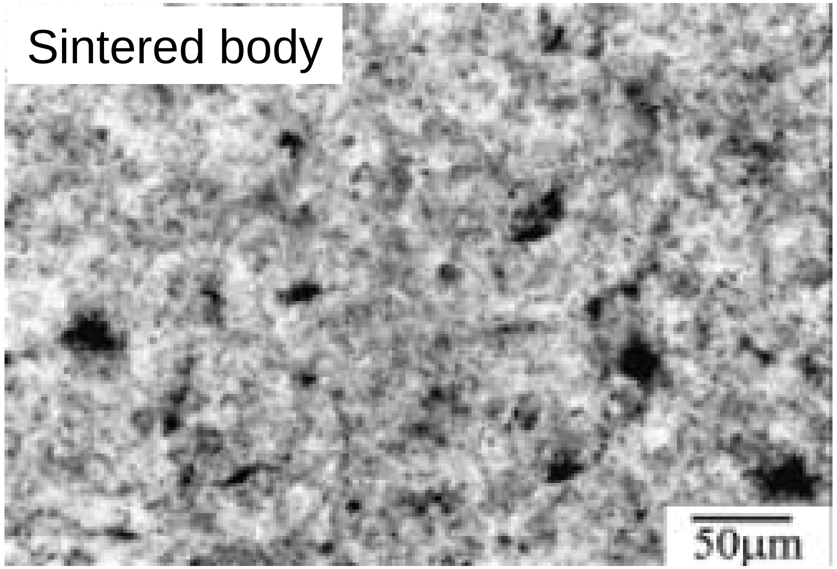
Al_2O_3 green body

Developed by Prof. Uematsu

Green body

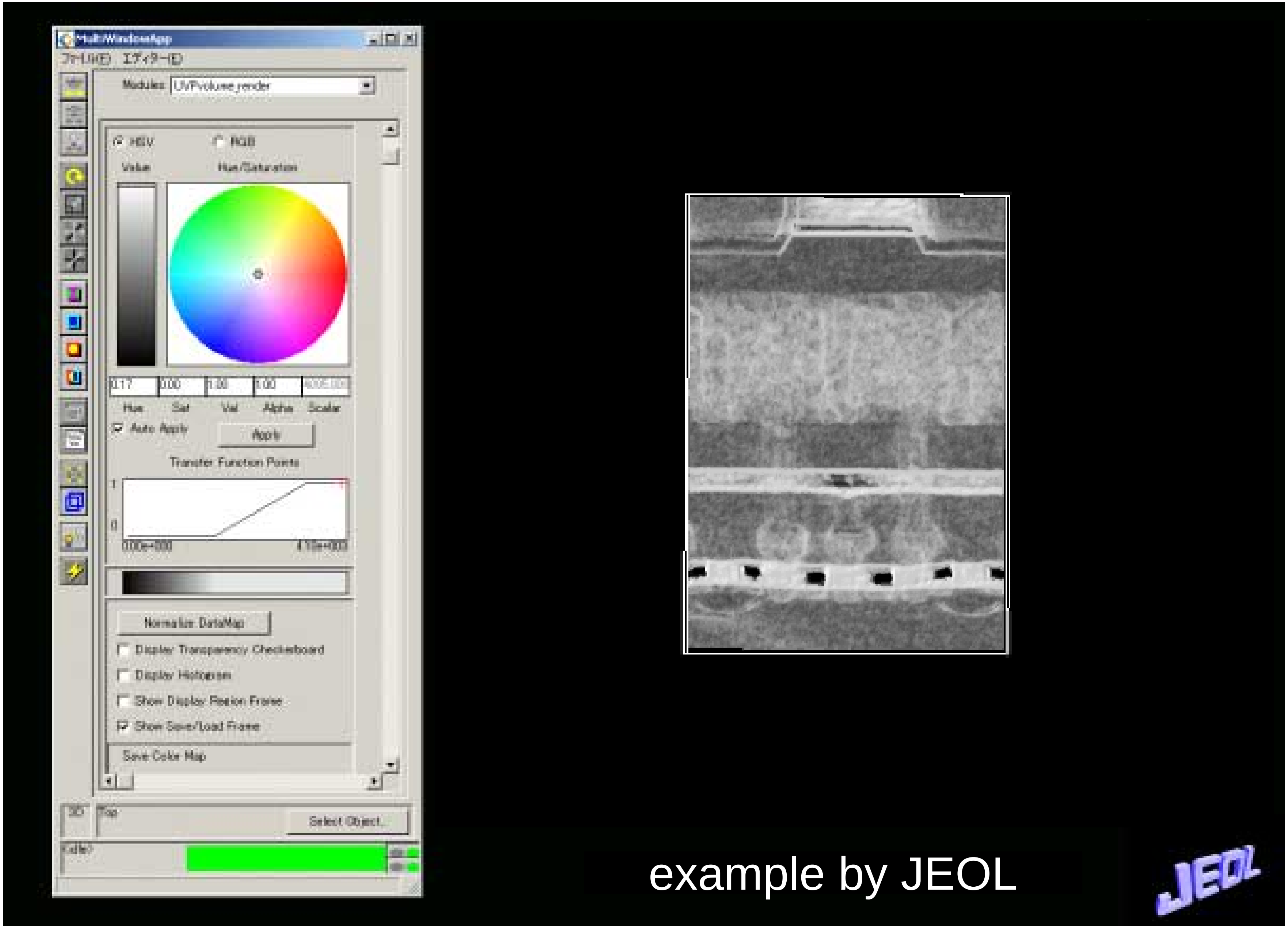


Sintered body



Digital optical microscope

TEM tomography (3D-TEM)



Modules: UVPvolume_render

● HSV ○ RGB

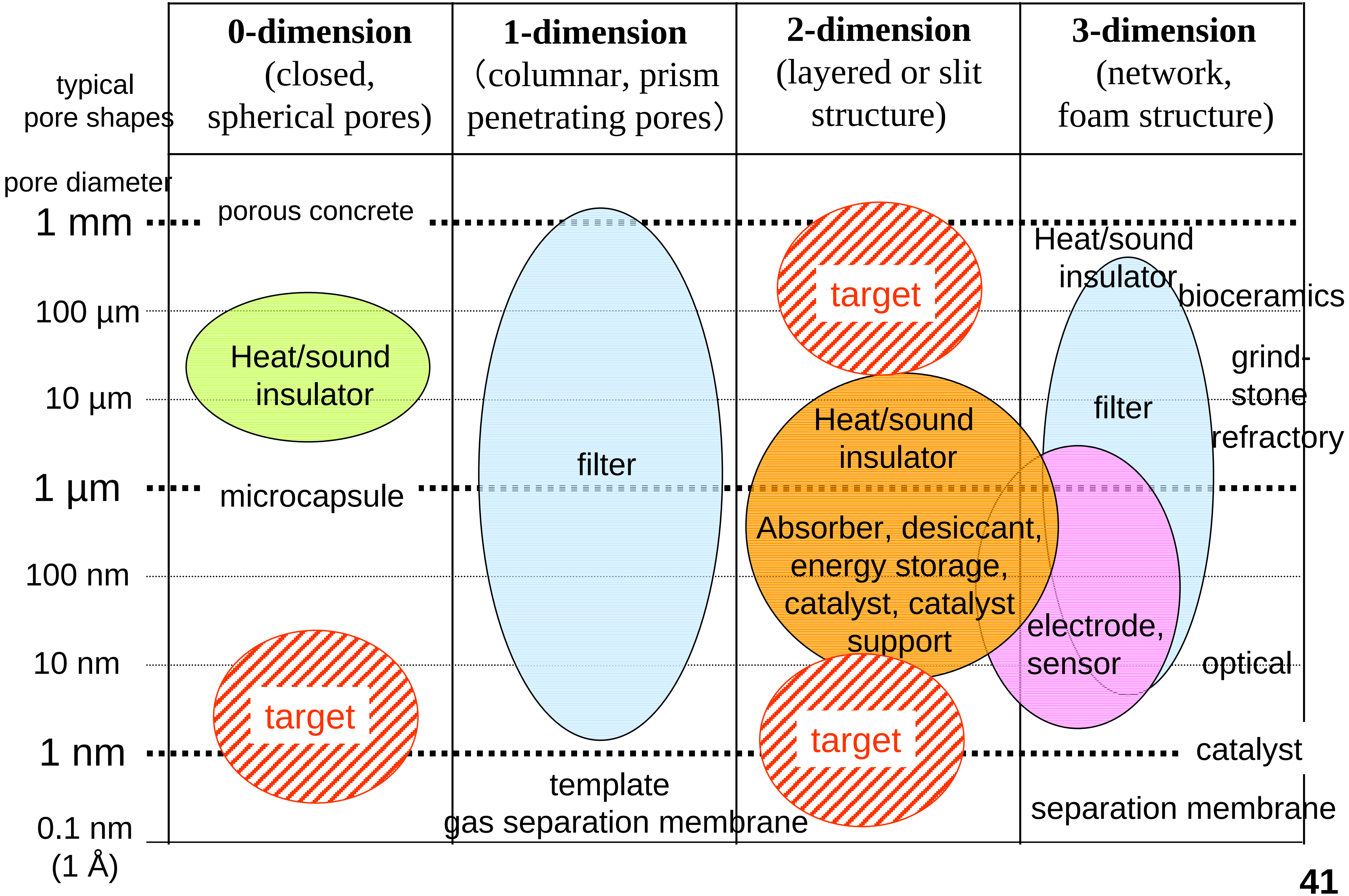
Hue	Sat	Val	Alpha	Scalar
0.17	0.00	1.00	1.00	[illegible]

☑ Auto Apply

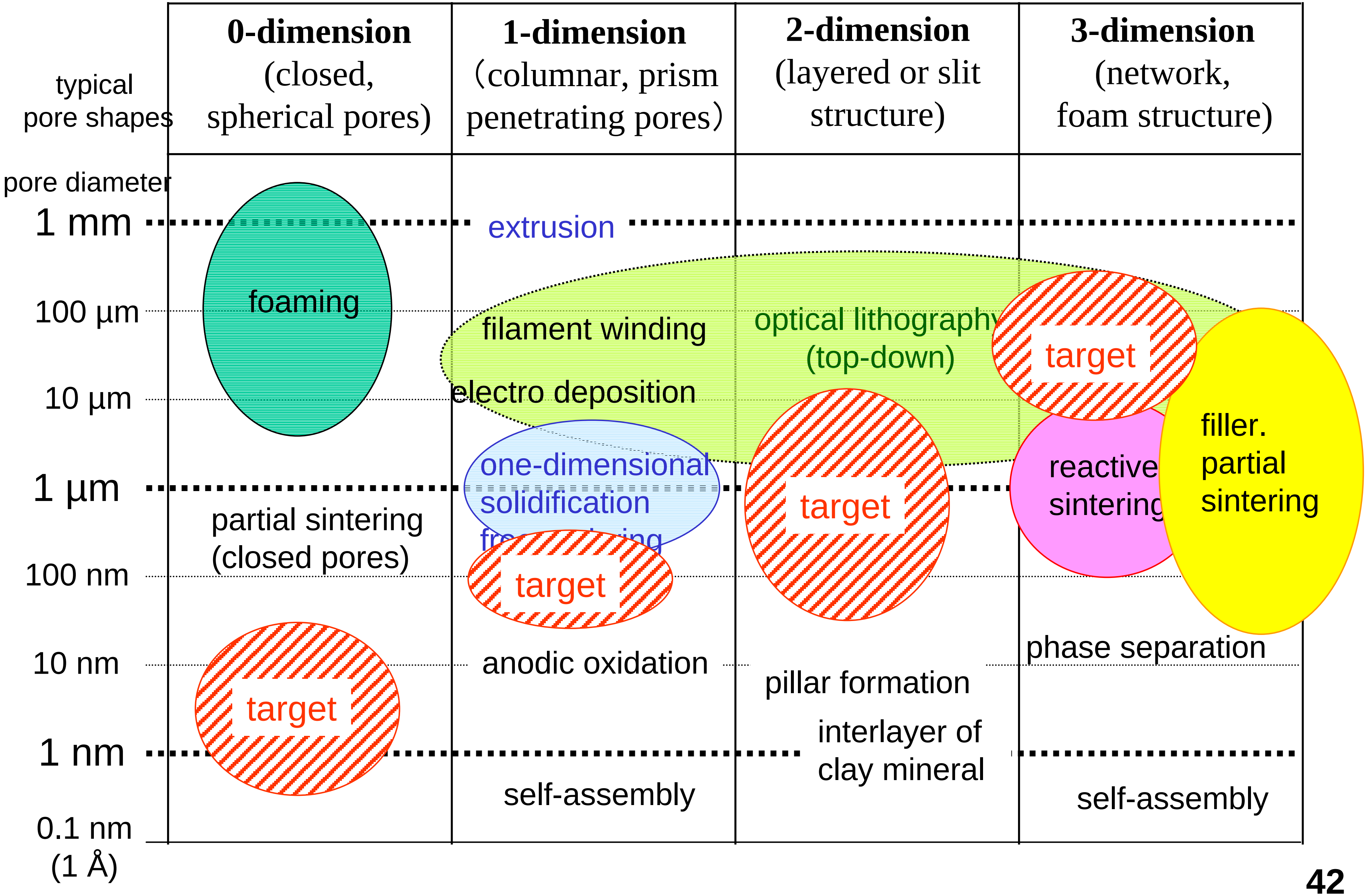
☐ Display Transparency Checkerboard
☐ Display Histogram
☐ Show Display Region Frame
☑ Show Save/Load Frame

example by JEOL

Porous materials map 1: Materials and applications



Porous materials map 2: Processes of porous materials



typical pore shapes

0-dimension (closed, spherical pores)

1-dimension (columnar, prism penetrating pores)

2-dimension (layered or slit structure)

3-dimension (network, foam structure)

pore diameter

1 mm

100 µm

10 µm

1 µm

100 nm

10 nm

1 nm

0.1 nm (1 Å)

extrusion

foaming

filament winding

electro deposition

optical lithography (top-down)

target

reactive sintering

filler. partial sintering

one-dimensional solidification

partial sintering (closed pores)

target

target

anodic oxidation

pillar formation

phase separation

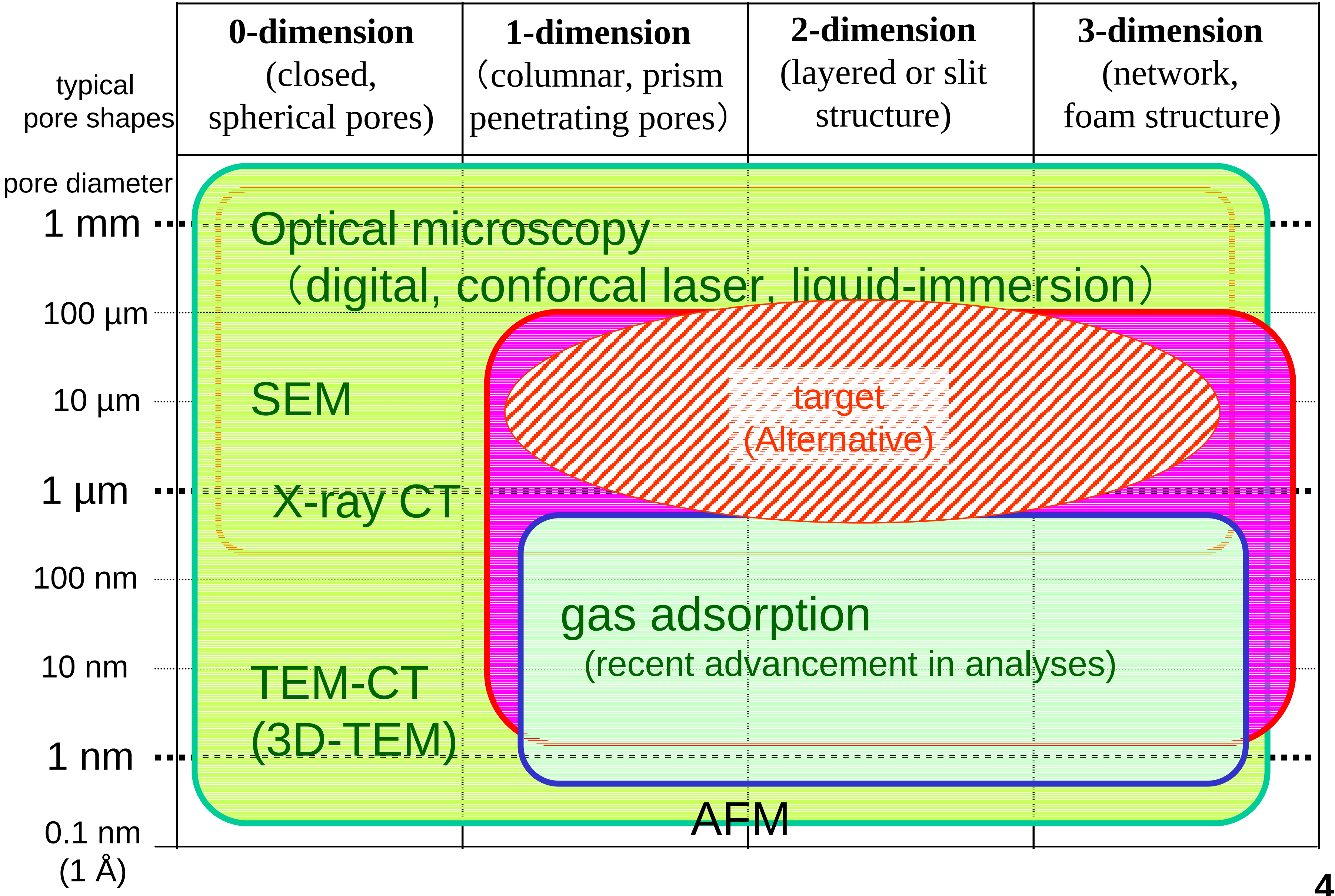
target

interlayer of clay mineral

self-assembly

self-assembly

Porous materials map 3: Analyses methods



In addition, SAXS, gas-permeation etc.

(c)Yoshikazu Suzuki

Hydrogen Energy and Fuel Cells

1. Hydrogen energy
    - Hydrogen
    - Hydrogen as secondary energy
    - Hydrogen production
    - Hydrogen storage / transportation
    - Hydrogen quiz

2. Fuel Cells
    - What is fuel cell ?
    - History of Fuel Cells
    - Types and technical principles
    - Future technologies
    - Fuel Cells quiz
    - Role-playing and SWOT analysis (as an excellent engineer!)

Hydrogen

Characteristics

- Isotopes and ratio (in atomic %)
  - ^{1}H 99.985 %
  - ^{2}H 0.015 % (Deuterium)
  - ^{3}H trace (half life 12.4 years, Tritium)
- Atomic weight 1.00794
- M.P. 14.01K, B.P. 20.28K
- Density 0.08988 kg/m^3 (gas, 273K)
- Clarke number 0.87 (No. 9)

order	elements	Clarke number
1	Oxygen	49.5
2	Silicon	25.8
3	Aluminum	7.56
4	Iron	4.70
5	Calcium	3.39
6	Sodium	2.63
7	Potassium	2.40
8	Magnesium	1.93
9	Hydrogen	0.83
10	Titan	0.46

Henry Cavendish

- Separated by Henry Cavendish, in 1766
- Named as "Hydrogen" by Antoine-Laurent de Lavoisier in 1783
- 1/14 of air weight
  Highest velocity of molecular movement
  High thermal conductivity (7 times higher than air) --> coolant
- Most abundant element in the universe.

H_2

H_2 gas

molecular weight	2.016
Density (at 15 ºC)	0.08376 kg/m^3 (1/14 of air)
Flash point	858 K (585 ºC)
flammability limits	4 - 75 vol% in air
energy density (per mass)	141.9 MJ/kg (per mass, highest among various fuels. 3 times of gasoline.)
energy density (per volume)	11.89 MJ/m^3 (as liquid H_2. Per volume, energy density is small, about 1/3 of gasoline)
Flame temperature in air	2318 K (2045 ºC)

Liquid H_2

used for rocket fuel

Boiling point	20.3 K (-252.8 ºC)
Density	70.8 kg/m^3 (0.0708g/cm^3) (at - 253 ºC) Compressible as 1/800 (in volume) compared with H_2 gas at STP.

History of hydrogen

1766 Separated by Henry Cavendish

1783 (1781) Named as "Hydrogen" by Lavoisier

1783/12 First manned balloon using H_2 gas

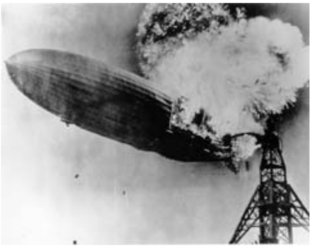
Jacques Charles (V/T = const): first pilotless balloon

Mass production of H_2 by waste iron + sulfuric acid

~1790 H_2 by carbonization of coal (England)

1912 Ammonia production by Haber–Bosch process

1937 Hindenburg Disaster



Actual cause was not by H_2 explosion but rather by static spark.
However, people start to consider the safe use of hydrogen from this accident.

Hydrogen as secondary energy

- No resource limitation in the future (produced from H_2O)
- After the use as fuel, product is only H_2O
- $H_2O \rightarrow H_2 \rightarrow H_2O$ cycle is faster than fossil fuels.
- Mass-storage is relatively easy than electricity.
- Fluid fuel for automobiles and airplanes (high energy density as ~300 % of gasoline per mass)
- Applicable for power generation by fuel cell
- Storage in the hydrogen-storing alloys

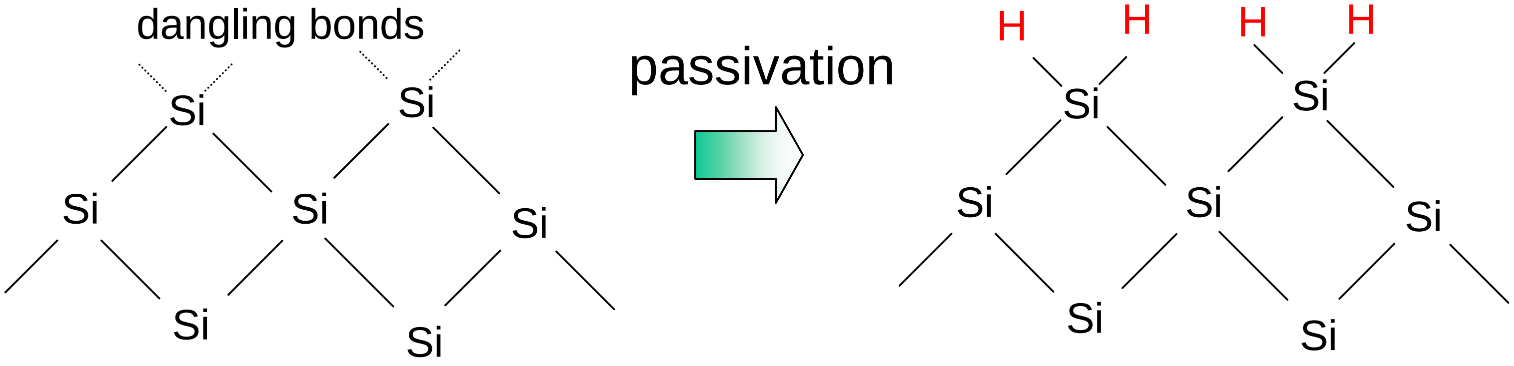
Present applications in chemical and semiconductor industories

- Raw materials for chemical industry

e.g $3\ H_2 + N_2 \rightarrow 2\ NH_3$ (ammonia synthesis)

unsaturated fatty acid (liquid) + $H_2 \rightarrow$ saturated fatty acid (solid)

- Surface passivation of Si semiconductor



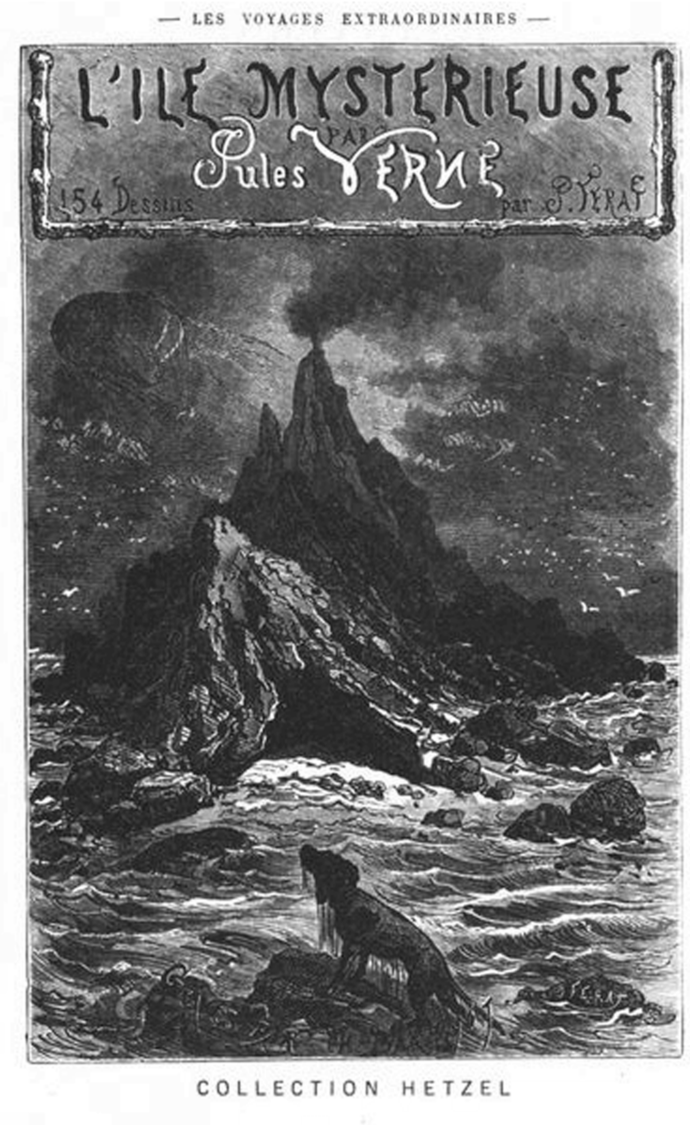
Hydrogen economy and Hydrogen society

- Instead of fossil fuels, hydrogen is used as energy "media". When the Oil crises occurred in 1970's, this "new" concept was spread.
- Since hydrogen energy is "secondary energy", renewable energies and next-generation atomic energies are expected to produce hydrogen.

- By-product water is drinkable.
  (in an average household, 5 kW/day equivalents to 6 L pure water.)

(figure from wikipedia)

L'Île mystérieuse (The Mysterious Island, by Jules Verne)



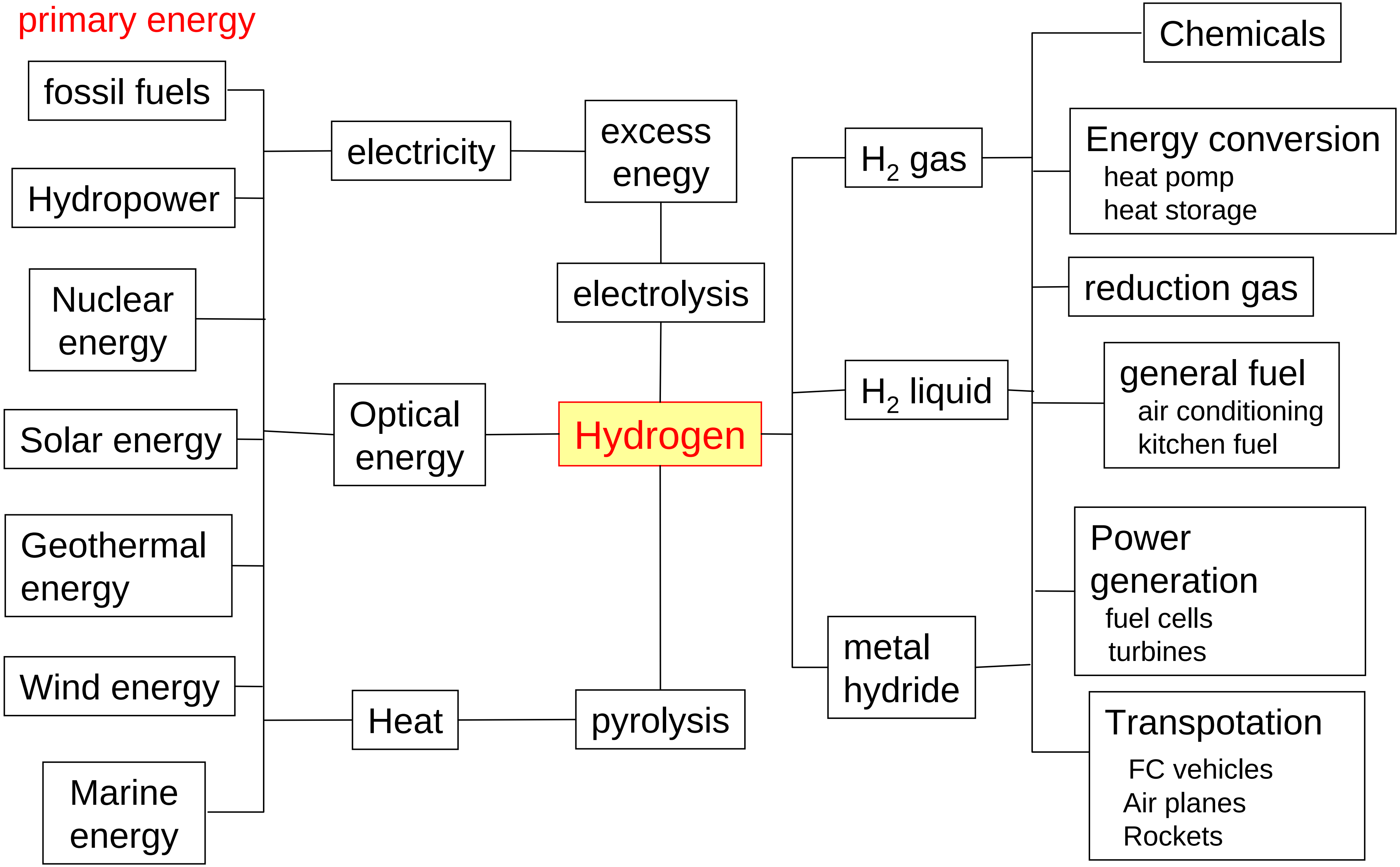
Adventure by Jules Verne, 1874.

"Water is decomposed into elements, and probably decomposed by electricity... and in someday, the decomposed products are used for fuels. Hydrogen and Oxygen, which compose H_2O, will offer exhaustless resources as energy with much stronger heat and light.

Water will be future coal."

Jules Verne: Known as
father of S.F., as well as
Herbert George Wells

Potential hydrogen energy system



by Oosumi Yasuaki, Clean energy / hydrogen

How to produce the hydrogen gas ?

From what ?	Fossil fuel, H_2O, biomass, waste
How ?	Gasification, thermal cracking, electrolysis, photolysis, biolysis
Where ?	Off-site: Hydrogen plant, by-product hydrogen On-site: reforming on the car, reforming within fixed fuel cell

World hydrogen production: 500 billion Nm^3/year (60 billion Nm^3 in EU15)

* Nm^3 : normal cubic meters (at 0ºC, 1 atm, an engineering unit)

about 97 %, produced from natural gas or petroleum at this moment

Water vapor reforming

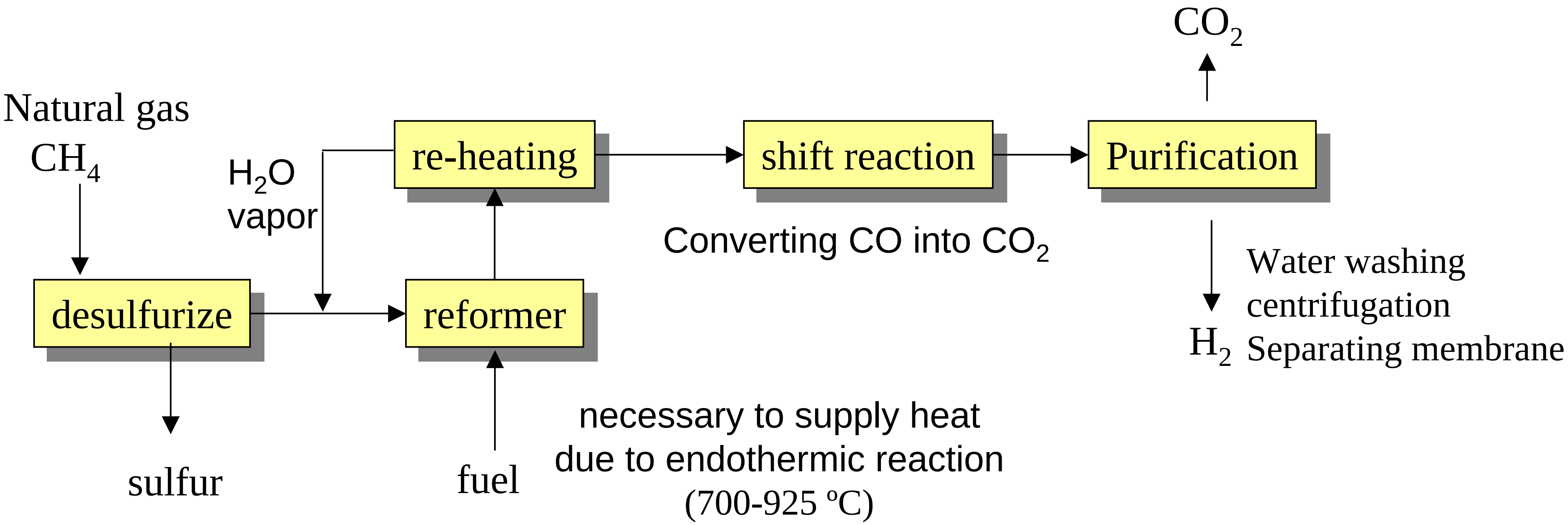
Hydrogen production from hydrocarbons

Reaction in a reformer

(1) $CH_4 + H_2O \rightarrow CO + 3H_2$ (production of "synthetic gas")

(2) $CO + H_2O \rightarrow CO_2 + H_2$ ("Water gas" conversion)

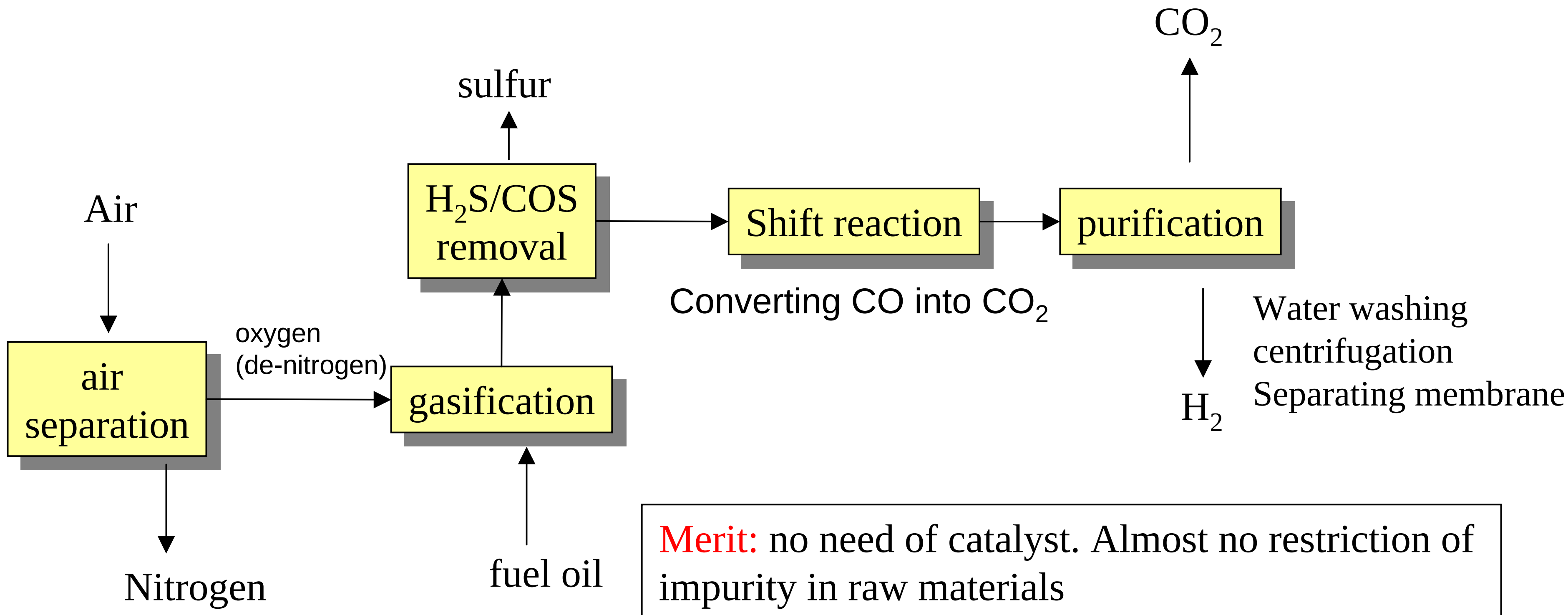
(3) $CO + 3H_2 \rightarrow CH_4 + H_2O$ (reverse reaction of (1))



Ni catalyst is used as reforming

Partial oxidation method

Applied for heavy hydrocarbons. Recently this method is also used for on-site reforming on the vehicles.



Converting CO into CO_2

Water washing
centrifugation
Separating membrane

Separation of H_2 from N_2 is difficult.
So, at first, nitrogen is removed from air,
and pure oxygen is used for partial oxidation.

Merit: no need of catalyst. Almost no restriction of impurity in raw materials

Demerit: higher reaction temperature. Expensive furnace materials (at 1100-1500°C)

Various hydrogen storages and transpotations

1. Compressed gas (soft steel cylinder) 150-200 atm

2. Compressed gas (CFRP) 350-700 atm (FC vehicles)

3. Hydrogen storing alloys and materials

4. Liquefaction

In the world, there are more than 30 pipelines to transport hydrogen or hydrogen/natural gas mixture. In particular, Ruhr region in Germany, soft-steel pipelines were operated since 1938. Until now, no accident.

Hydrogen storage / transportation

storage types	kg H_2/kg (per mass)	kg H_2/m^3(per volume)
Large scale		
Storage in underground space		5-10
Compressed gas (on the ground)	0.01-0.014	2-16
Metallic hydride	0.013-0.015	50-55
Liquid hydrogen	~1	65-69
Fixed small scale（1-100 m^3）		
Compressed gas in cylinder	0.012	~15
Metallic hydride	0.012-0.014	50-53
Liquid hydrogen	0.15-0.50	~65
On the vehicles（0.1-0.5 m^3）		
Compressed gas in cylinder	0.05	15
Metallic hydride	0.02	55
Liquid hydrogen	0.09-0.13	50-60

Hydrogen Quiz

Q. 1/6

Energy density per mass of the hydrogen is the best among various fuels. About _____% of gasoline.

Energy density per volume of the hydrogen is small.Even for liquid H_2, it is about ______of gasoline.

Q. 2/6

"Clarke number" (weight % of element in the surface of earth) of hydrogen is ~ 0.83. This is the ___th among all elements.

In the universe, hydrogen is ______________element.

Q. 3/6

Flammability limits: - vol% in air (Very wide !!)

Hydrogen Quiz

Q. 4/6

First manned balloon using H_2 gas was oparated by French chemist,_______________ , and Robert brothers.

Q. 5/6

Hydrogen energy system was first written in S.F. by ________________ (father of S.F.).

Then, hydrogen society was actually attracted much attention in ______'s due to the oil crises. After 2000's, thanks to fuel cell technologies, the hydrogen society might be realized...

Q. 6/6

Recently, _________atm cylinder for FCV has been developed to increase the travel distance.

Types of batteries

- Chemical
  - Disposable
  - Rechargeable
  - **Fuel Cells**
    - **Alkaline fuel cell (AFC)**
    - **Phosphoric acid fuel cell (PAFC)**
    - **Molten carbonate fuel cell (MCFC)**
    - **Solid oxide fuel cell (SOFC)**
    - **Polymer electrolyte fuel cell (PEFC)**
- Physical
- Biological

Fuel cell

“A fuel cell is an electrochemical energy conversion device. It produces electricity from various external quantities of fuel (on the anode side) and an oxidant (on the cathode side).“

Example of the reactions

Anode：Oxidation $H_2 \rightarrow 2H^+ + 2e^-$

Cathode：Reduction $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

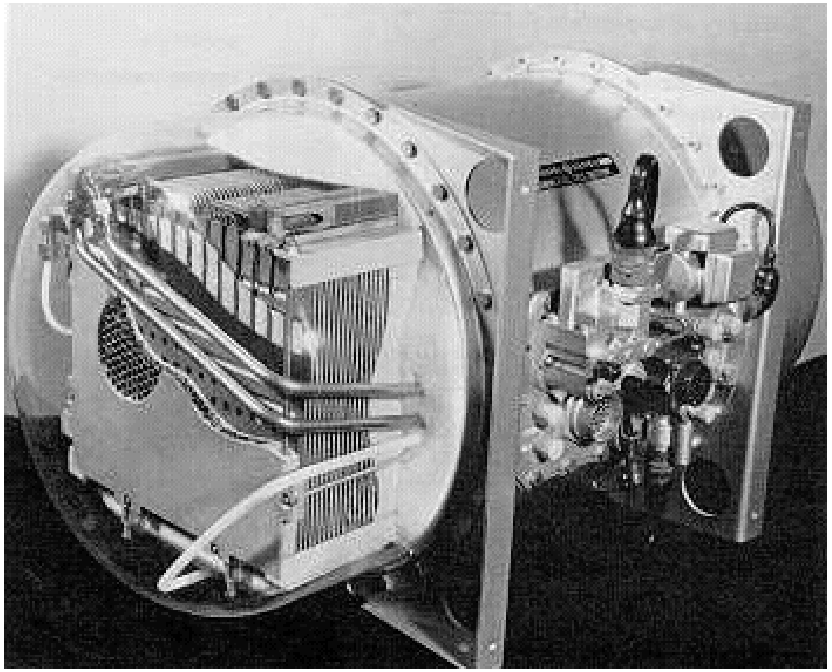
(total reaction is : $H_2 + 1/2O_2 = H_2O$）

History of fuel cells

”Father of fuel cell"

In 1839, first fuel cell was demonstrated by Sir William Robert Grove (Wales).

Gemini project in 1960's. (the first commercial use of a fuel cell)



PEFC in Gemini spaceship

Technical merits

High efficiency by direct conversion from chemical energy to electricity

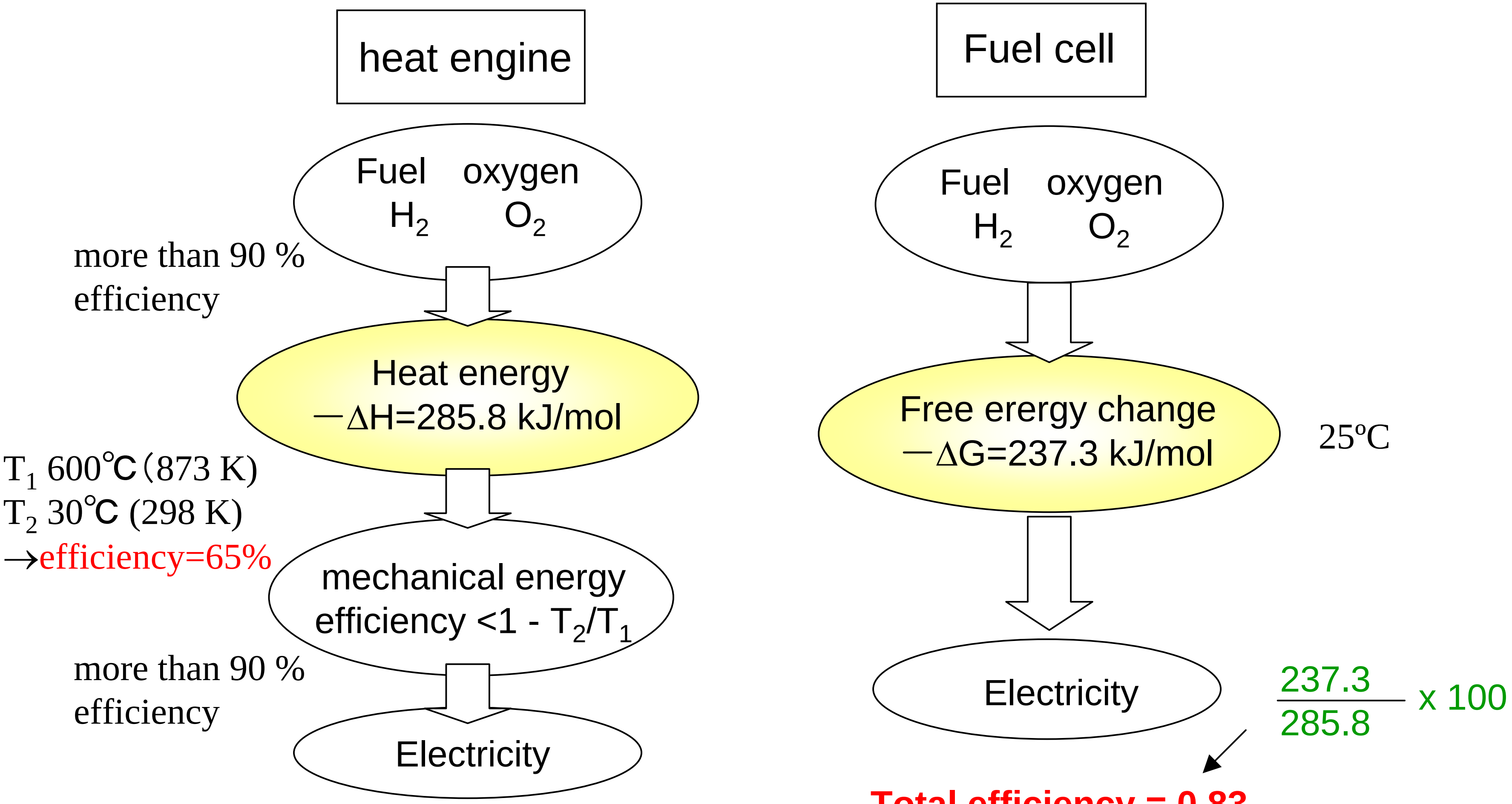
Heat engine: Heat → Mechanical energy → electricity
(vapor/gas)

Carnot cycle for heat engine: energy efficiency = $1-T_2/T_1$

T_1 : input temperature
T_2 : output temperature

Fuel cell: Chemical energy → electricity

Energy efficiency (to convert into electricity)



heat engine

Fuel oxygen
H_2 O_2

more than 90 %
efficiency

Heat energy
$-\Delta H=285.8$ kJ/mol

T_1 600℃ (873 K)
T_2 30℃ (298 K)
→efficiency=65%

mechanical energy
efficiency $<1 - T_2/T_1$

more than 90 %
efficiency

Electricity

Fuel cell

Fuel oxygen
H_2 O_2

Free erergy change
$-\Delta G=237.3$ kJ/mol

25ºC

Electricity

$\frac{237.3}{285.8} \times 100$

Total efficiency = 0.83

Total efficiency ＜0.65 (actually 0.4-0.5)

Recent co-generation technology enables to use waste-heat.So, total energy efficiency can be ~ 80 %.

Classification of fuel cells

Type	**Alkaline (AFC)**	**Phosphoric acid (PAFC)**	**Molten carbonate (MCFC)**	**Solid oxide (SOFC)**	**Polymer electrolyte (PEFC)**
Temperature	5-240ºC	160-210ºC	600-700ºC	900-1000ºC	60-80ºC
Electrolyte	KOH	Conc. H_3PO_4	Li_2CO_3 K_2CO_3	ZrO_2 (Y_2O_3)	cation-exchange membrane
Anode	pure H_2 (no CO_2)	H_2	H_2, CO	H_2, CO	H_2
Cathode	pure O2 (no CO_2)	Air	Air	Air	Air
Carrier	OH^-	H^+	CO_3^{2-}	O^{2-}	H^+
Actual efficiency for generation of electricity	50-60%	40-45%	45-60%	50-65%	35-40%
Applications	space plane	On-site, separate battery	Mass production	Mass production	On-site, mobiles

slow reaction at electrodes

Theoretical efficiency at different temperatures

Reaction: H_2 (g) +1/2O_2 (g) = H_2O (g)

Table for H_2O (g) as the product

PEFC
AFC, PAPC
MCFC
SOFC

Temperature (ºC)	ΔHº (kJ/ mol)	ΔGº (kJ/ mol)	Efficiency (η)
25	-241.8	-228.6	0.945
200	-243.5	-220.4	0.905
400	-245.3	-210.3	0.857
600	-246.9	-199.7	-0.809
800	-248.2	-188.7	0.760
1000	-249.3	-177.5	0.712

Thermodynamically, efficiency of FC becomes higher when operated at low temperature.
But kinetically, at low temperature, electrode reactions becomes slow. (actual efficiency)

Electromotive force, EMF

$H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O\ (l)$, $-\Delta G = 237.3$ kJ/mol (25°C)

EMF $E^o = -\Delta G^o / nF = 237300\ [J/mol] / (2 \times 96500\ [C/mol])$

$= 1.23\ [J/C] = 1.23\ [V]$

STP

number of electrons in this reaction
(2 electron reaction)

Anode：Oxidation $H_2 \rightarrow 2H^+ + 2e^-$

Cathode：Reduction $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

On of the disadvantage of the H_2-O_2 fuel cell system, that is low EMF (1.23 V).

So, for the actual power generation purpose, tens to hundreds FC are connected in series → stacks

Exercise: EMF of CH_4 gas fuel cell ?

For the house-use fixed fuel cell, CH4 gas is used as a fuel. Suppose without converting to H2, and direct oxydation of CH_4 is used as the fuel cell reaction, what is the EMF value ?

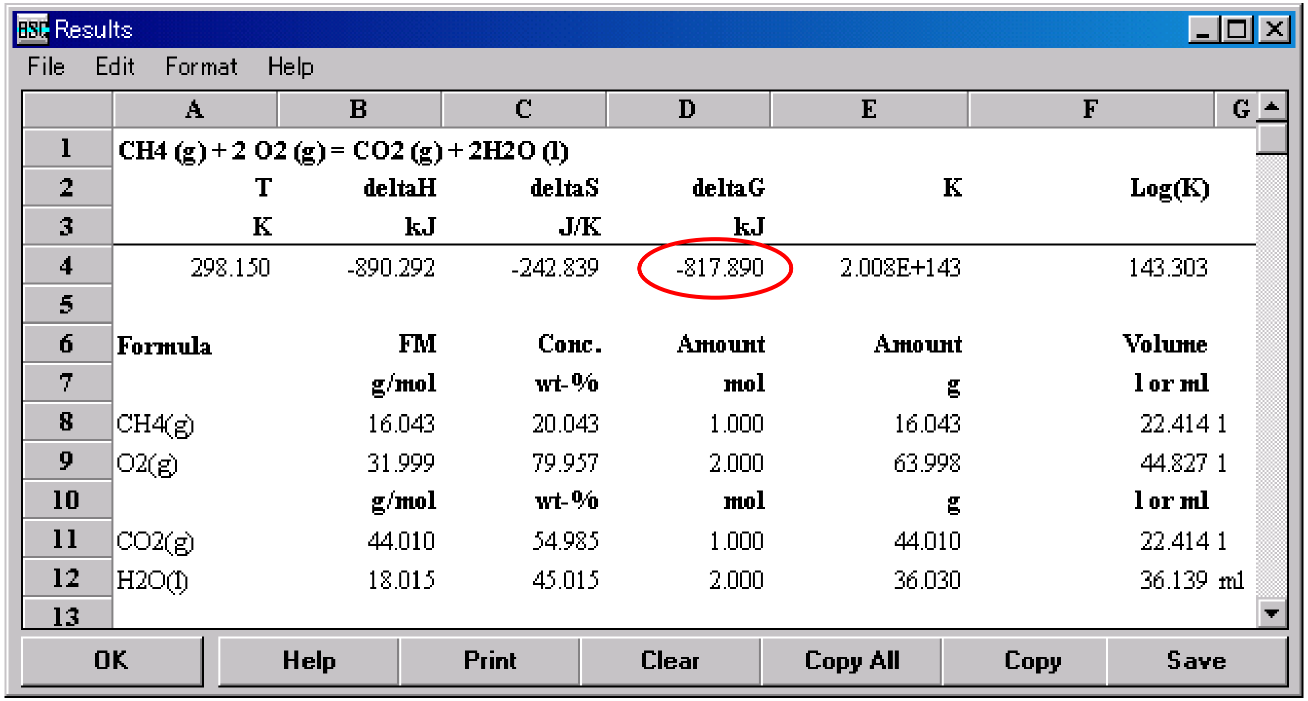
CH_4 (g) + 2 O_2 (g) = CO_2 (g) + $2H_2O$ (l) $\Delta G^o = -\ 817\ \mathrm{KJmol^{-1}}$ (298K)

In this reaction of 1mol CH_4, 4 oxygen atoms (oxidation state of 0) change into oxide ions (oxidation state of -2). i.e., "8 electron reaction".

$$E^\circ = -\Delta G^o / 8F$$

$$= \frac{817000\ \mathrm{Jmol^{-1}}}{(8 \times 96500\ \mathrm{C\ mol^{-1}})}$$

= **1.06 V**



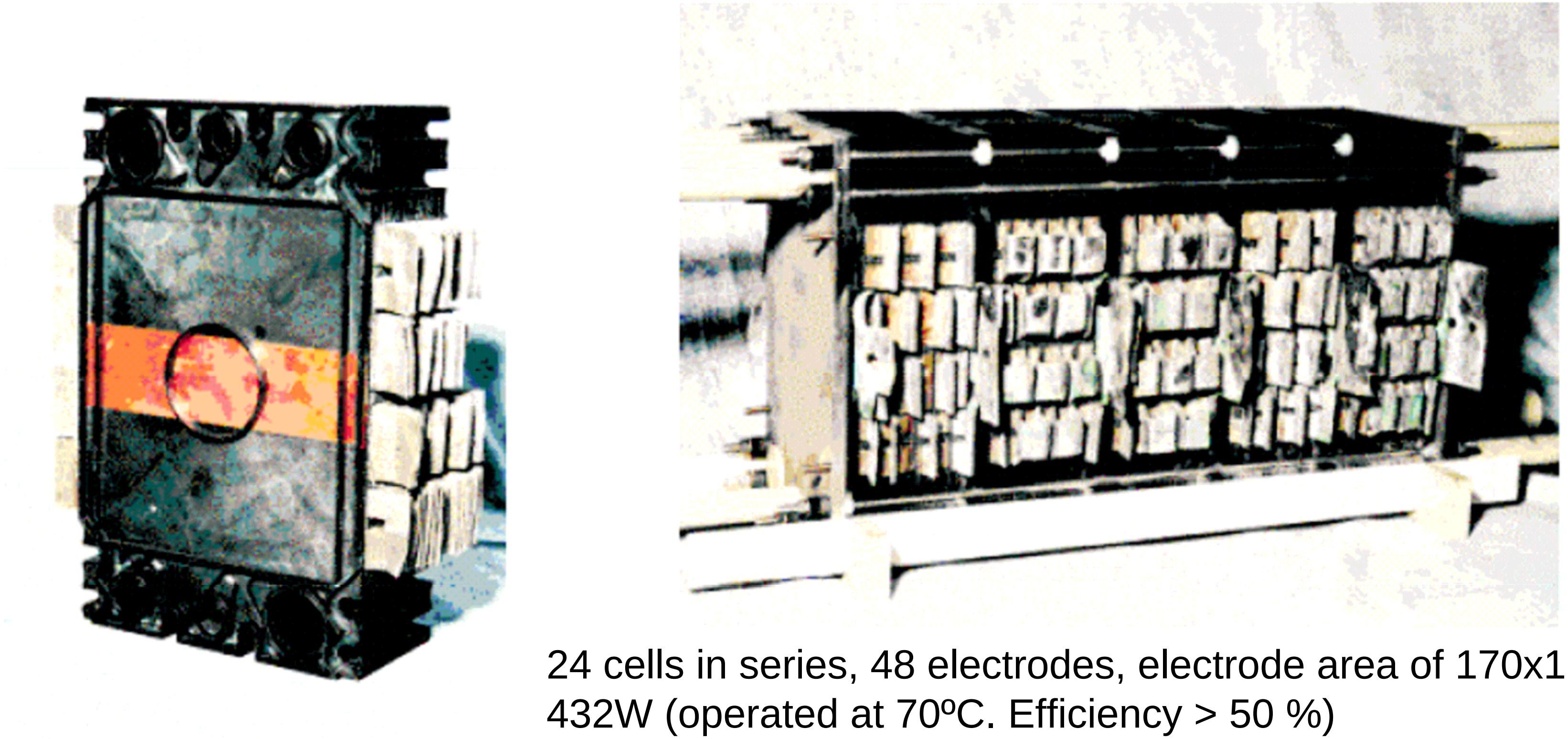
	A	B	C	D	E	F	G
1	CH4 (g) + 2 O2 (g) = CO2 (g) + 2H2O (l)						
2	T	deltaH	deltaS	deltaG	K	Log(K)	
3	K	kJ	J/K	kJ			
4	298.150	-890.292	-242.839	-817.890	2.008E+143	143.303	
5							
6	Formula	FM	Conc.	Amount	Amount	Volume	
7		g/mol	wt-%	mol	g	l or ml	
8	CH4(g)	16.043	20.043	1.000	16.043	22.414 l	
9	O2(g)	31.999	79.957	2.000	63.998	44.827 l	
10		g/mol	wt-%	mol	g	l or ml	
11	CO2(g)	44.010	54.985	1.000	44.010	22.414 l	
12	H2O(l)	18.015	45.015	2.000	36.030	36.139 ml	
13							

Alkaline fuel cell (AFC)

E. De Geeter et al. / Journal of Power Sources 80 (1999) 207–212

High efficiency. However, due to the reaction between electrolyte and CO2, the use is very limited (e.g., in outer space)

CO_2 must be removed from operating conditions



24 cells in series, 48 electrodes, electrode area of 170x170 mm
432W (operated at 70ºC. Efficiency > 50 %)

Fig. 3. Module and assembly of modules to form a fuel cell stack.

Alkaline fuel cell (AFC) system

E. De Geeter et al. / Journal of Power Sources 80 (1999) 207–212

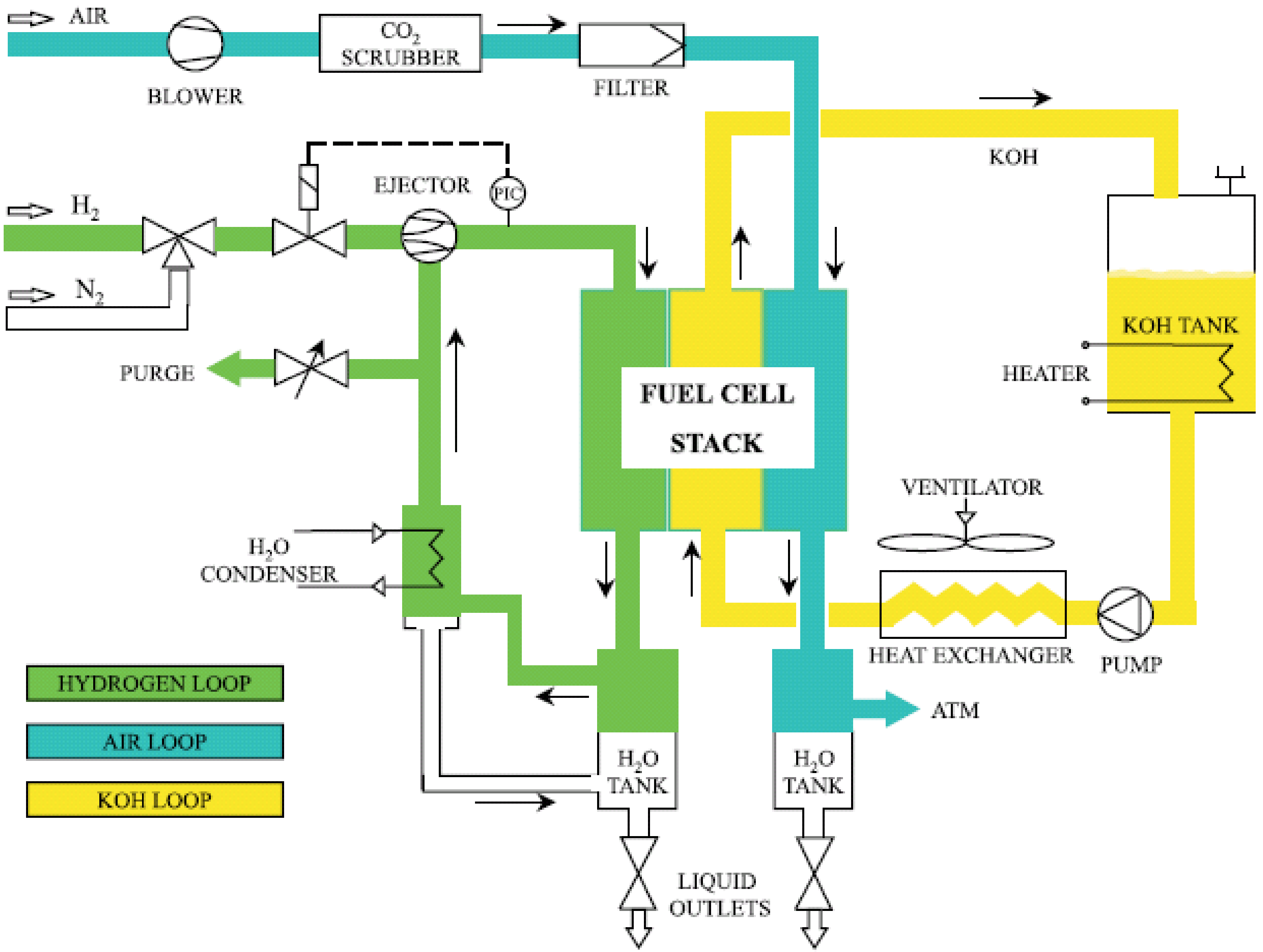


Fig. 4. Fluid flows in the AFC system.

Why high-temperature FCs are needed?

Thermodynamically, efficiency of FC becomes higher when operated at low temperature.

But kinetically, at low temperature, electrode reactions becomes slow. (actual efficiency)

So, in the "real" power-generation purpose,

- At high temperatures, electrode reactions become rapid.
  (i.e. no need of very expensive catalysts as Pt, Pd and Ru)
- Quality of waste heat becomes better.
  (in the view point of available energy, or "exergy"

⇩

Molten carbonate fuel cell (MCFC) at 600-700ºC
Solid oxide fuel cell (SOFC) at 900-1000ºC

- Too high temperatures (>1000ºC) need other expensive materials.

Molten carbonate FC

In the end of 19 century and the beginning of 20 century, KOH (mp. 380ºC) and NaOH (mp. 318ºC) were used as molten salt for fuel cell.

However, they easily react with CO_2 in air. So, the power generation was soon terminated.

We can learn something!

Using carbonates as molten salt, CO_2 in air became harmless.

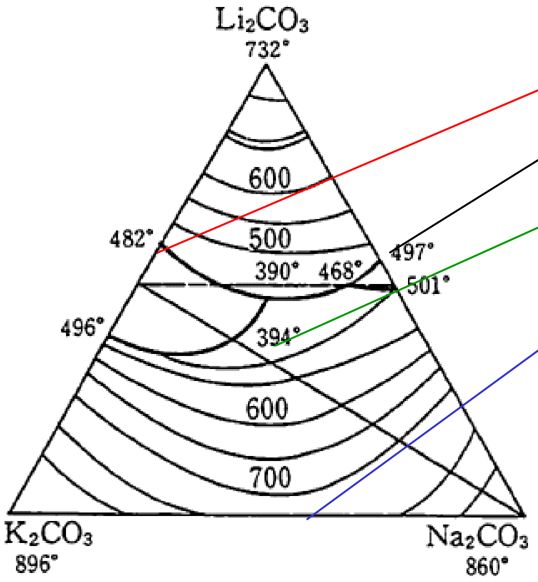
Required characteristics for molten carbonate at operating temperature

1) Chemically stable
2) High conductivity
3) Low vapor pressure
4) Inert for electrodes and other materials
5) Cheap

Alkali carbonate, such as Li_2CO_3, Na_2CO_3 and K_2CO_3.
Using these mixture, melting point becomes low, and conductivity becomes high

Mixing effect of alkali carbonates

alkali carbonates	compositions	melting points (°C)
Li_2CO_3		720
Na_2CO_3		850
K_2CO_3		901
Li_2CO_3-Na_2CO_3	53.3 : 46.7	496
Li_2CO_3-K_2CO_3	62.0 : 38.0	488
Na_2CO_3-K_2CO_3	42.7 : 57.3	710
Li_2CO_3-Na_2CO_3-K_2CO_3	43.5 : 31.5 : 25.0	397



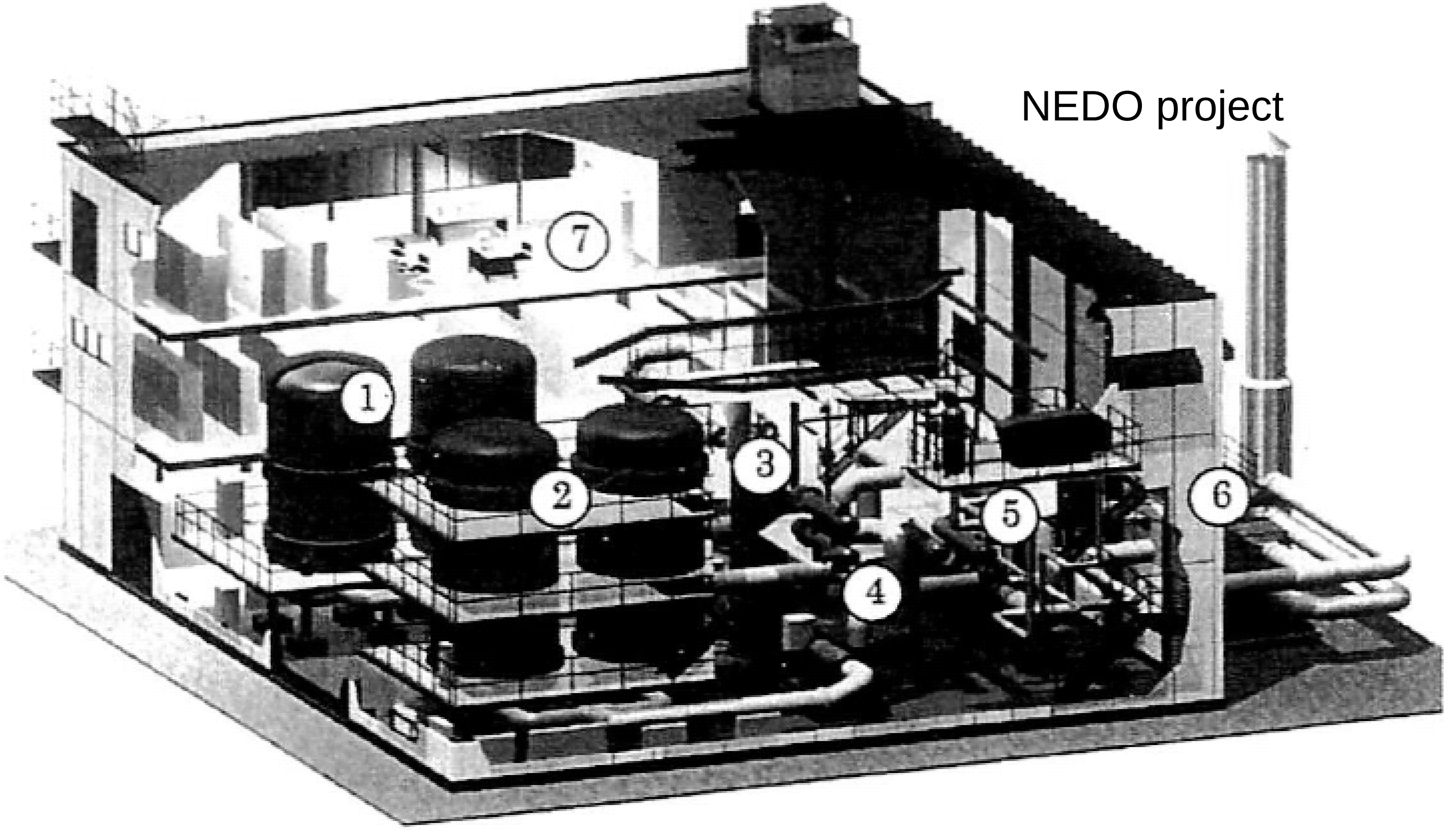
mixing several carbonates decreases melting point.

In Japan Li-Na system is usually used due to the inertness against the electrodes.

$LiAlO_2$ ceramic tile soaks the molten salt.

1 MW power-plant by Molten Carbonate Fuel Cell (MCFC)

Tested in 1993-1999



NEDO project

1), 2) 250 kW cell stack
3) reformer
4) High-pressure Blower for cathode (air) circulation
5) Turbine Compressor
6) Waste-heat boiler
7) Central control room

First commercial MCFC power plant

300 kW, in Chubu electric Power Co.

Waste gas can be used as fuel (without catalyst, i.e., no damage for expensive catalyst)

http://www.chuden.co.jp/corpo/publicity/press2002/0918_1.html

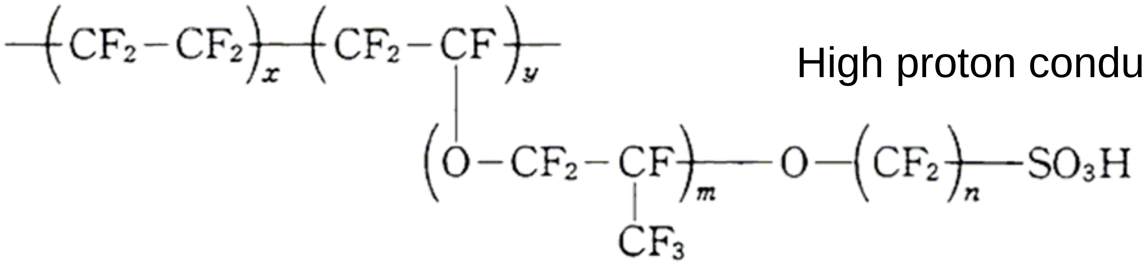
Solid oxide fuel cell (SOFC)

- All solid (no use of liquid in the cell)
- No need of fuel-reformer (only fuel and air are needed)
  → Impressing like as "Silent generator" rather than chemical battery
- Operation temperature is 700-1000ºC. Due to the high quality of waste heat, total energy efficiency becomes high by using co-generation.
- Several kW for household
- Several hundreds kW for separated power source.

Solid electrolyte	Composition	Charecteristics
Zirconia ~ 1000ºC	$(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ $(ZrO_2)_{0.94}(Y_2O_3)_{0.06}$	High chemical stability High mechanical strength Relatively non-expensive
Ceria ~ 700ºC	$(CeO_2)_{0.9}(Sm_2O_3)_{0.1}$ $(CeO_2)_{0.9}(Gd_2O_3)_{0.1}$	High conductivity Easy to be reduced at HT Low mechanical property
Perovskite	$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$	High conductivity Resistant to reduction High reactivity with others

Polymer electrolyte FC (PEFC)

- Developed in 1960s by GE.
- Currently, most common fuel cells (for FCV etc.)
- Low operating temperature (~ 80ºC): No need for start up.
- Compact.
- Ion-exchanging membrane (such as Nafion ®, by DuPont) is used.



High proton conductivity

Anode：Oxidation $H_2 \rightarrow 2H^+ + 2e^-$

Cathode：Reduction $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

(same as phosphoric acid fuel cell)

Direct methanol fuel cell (DMFC)

- Without reforming, methanol is directly used as a fuel.
- Applied for mobile computer and cellular phones.

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $6H^+ + 3/2O_2 + 6e^- \rightarrow 3H_2O$

Total reaction: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$

http://allabout.co.jp/computer/notepc/closeup/CU20070214F/index2.htm)

$-\Delta G^o = 702.8$ kJ/mol

$$E^o = 702800\ [J/mol] / (6 \times 96500\ [C/mol]) = 1.21\ [V]$$

Similar EMF value as hydrogen fuel cell. However, due to the "Crossover" actual EMF becomes lower.

DMFC in Guinness records

CERTIFICATE

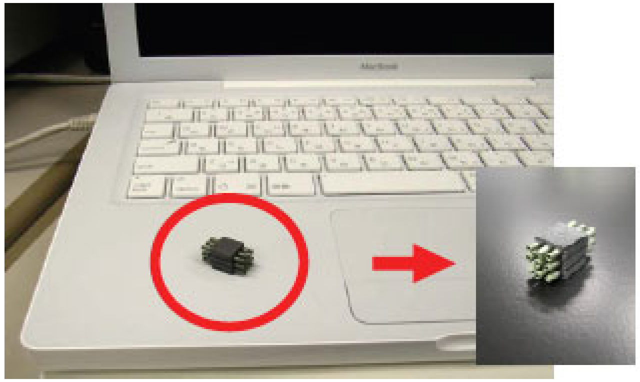
The smallest direct methanol
el cell measures 22 x 56 x 4.5 mm
(0.87 x 2.2 x 0.18 in).

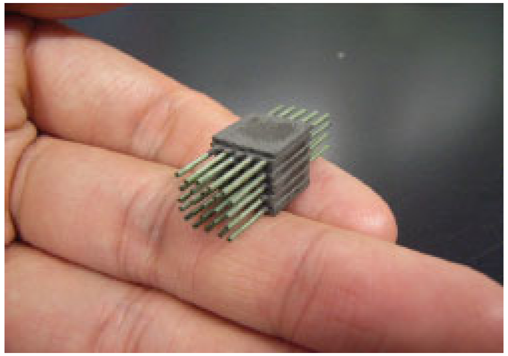
22 mm (width) x 56 (length) x 4.5 mm (thickness), 8.5 g, 100 nW
by Toshiba, in 2006 Guinness book (Smallest DMFC)

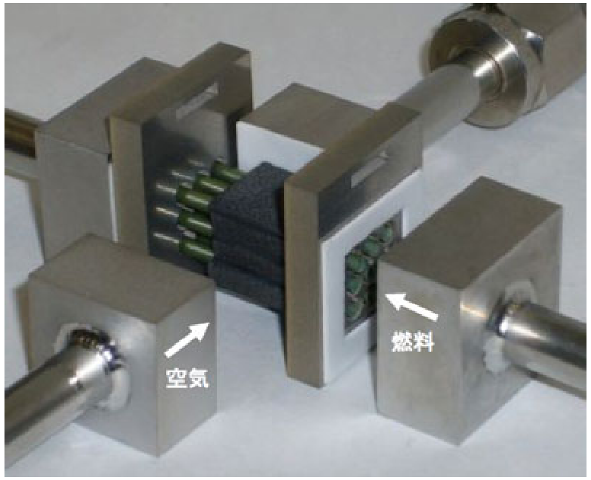
Toshiba review Vol. 62 [6] (2007)

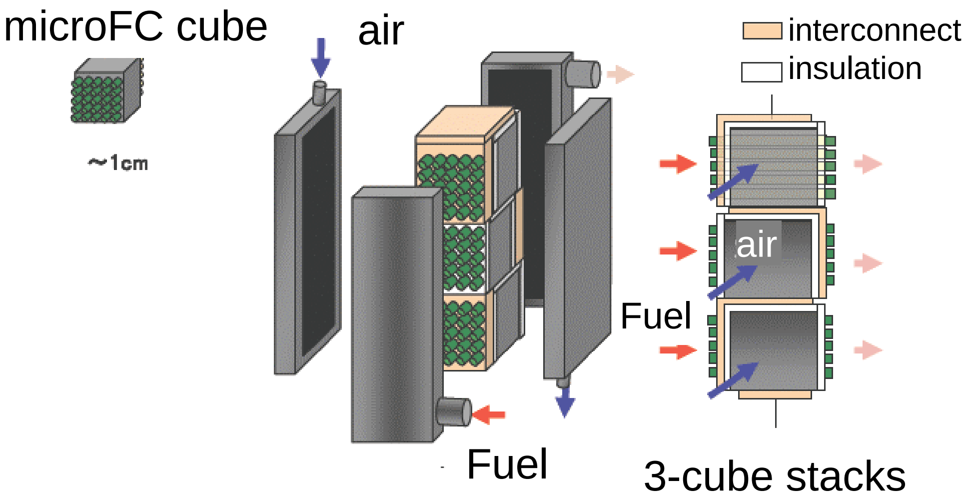
Future fuel cell technology

Ultra small, high power-density micro FC (AIST / FCRA / NGK-NTK)
 > 2W output by 1cm^3 fuel cell (operated at < 600ºC)









http://www.aist.go.jp/aist_j/press_release/pr2007/pr20070329/pr20070329.html

Fuel cell quiz

Q. 1/6

In batteries, when discharging (i.e., actual using),
Electrode with oxidation is called as "__________"
Electrode with reduction is called as "__________"

Q. 2/6

In 1839, first fuel cell was demonstrated by__________________ .

Q. 3/6

For fuel cells, different from heat engines, there is no limitation by ________cycle. So, fuel-to-electricity conversion efficiency is potentially high.

Q. 4/6

EMF of hydrogen-fuel cell is theoretically ______V.

Q. 5/6

For PEMC, proton conductive membrane is necessary.
One of the most famous and common membrane is "__________" by Du Pont, developed in 1962.

Q. 6/6

EMF of DMFC is theoretically ______V. However, due to the ___________ effect, actual EMF becomes lower.

Planing meeting simulation on "Fuel-cell mobile phones"

Setting: End of 2008...Toward the coming Christmas market in 2010, XXX company plans to put "Fuel-cell mobile phones" into the real market. Up to now, various technical problems have been already solved. Cost is probably OK. Competitor might have a similar strategy... Still, There are many problems to be solved.

Participant express the opinions according to the role.

Mobile phone supplier (XXX company)

- CTO / Director of the development (Confident on the technologies of own company).
- Representative Engineer (Detailed knowledge of own technologies (good and bad points)
- Director on marketing (FC phone as a strategic product in the company.)
- Product designer (product and package design)
- Internal copywriter (have a nice copy)
- Director of Legal & Compliance division (against taking risks)
- CEO (neutral and calm-headed)

Carrier company (YYY phone)

- Planner (positive, e.g., initiative on new technology)
- Planner (negative, e.g., product safety)
- Director (Charge in Retail sale, neutral and very cool-headed)

Retail

- Hypermarket in Europe (Dealing with YYY phone. But they want to be "low-risk high return")
- Advertising agency

SWOT analysis on the "Fuel-cell mobile phones"

ITems	Outline
Target	**Fuel-cell mobile phones**
Present state and problems	
Needed technology	
Business strategy	
Scenario on technical development	(1st year)
	(2nd year)
	(3rd year)
	(5th year)
Secondary (derived) technology	
Comments / notes	

SWOT analysis on the "Fuel-cell mobile phones"

2. Current status analysis

2-1: Strong and weak points compared with the competitor (competitor:)

Items	Outlines	*	* Evaluation in 5 ranks
Product quality			
Production cost			Compared with competitor: 5: Very superior 4: superior 3: equivalent 2: inferior 1: Very inferior
Human resource for development and production			
Distribution (how broad range)			
Distribution speed			
Patent right			
Brand value			
Sales promotion			
Sales staffs			

SWOT analysis on the "Fuel-cell mobile phones"

2-2: Threat on this business (Outer factors)

Items	**Outlines**	*	* **Evaluation in 3 ranks**
Competitor			3:Serious threat 2: Threat 1: No threat
New competitor			
Competition in distribution			
Stock (purchasing raw materials)			
Barriers to entry			
Price competition			
Increasing segments			

SWOT analysis on the "Fuel-cell mobile phones"

2-3 Opportunity for own company (business chance)

Items	**Outlines**	*	* **Evaluation in 3 ranks**
Market size, Market growing rate			3: Big opportunity 2: opportunity 1: No opportunity
Technical change			
Unsatisfied needs			
Profitability			
Less competitor			
Barriers to new entry of own company			
stable price			

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