Proton conduction in glass and its application to fuel cell

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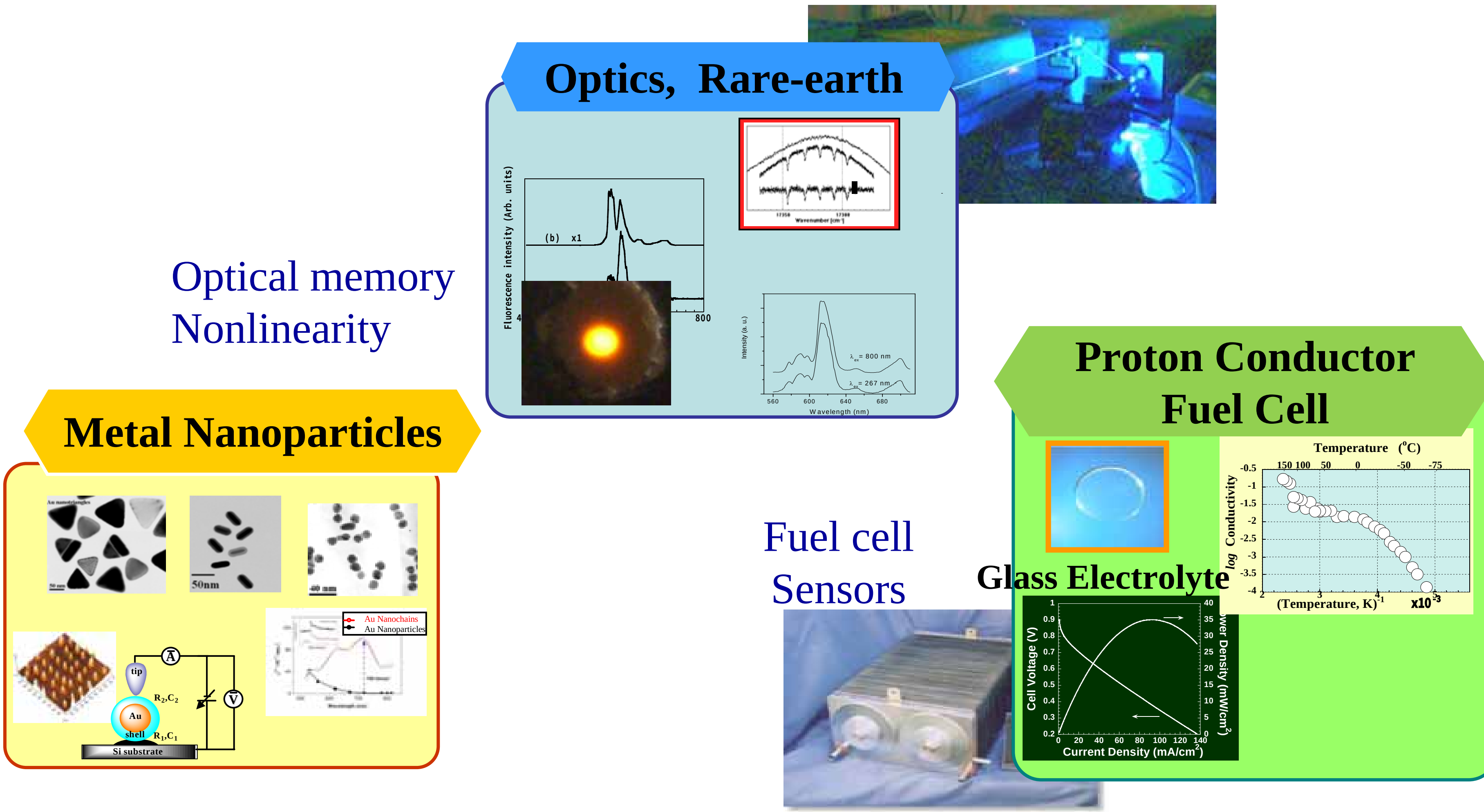
★ **New optical glasses**

★ **Fast proton conducting glasses and their application to fuel cell**

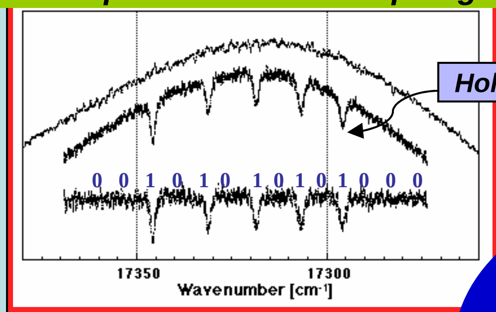
★ **Self-assembling of nanoparticles**



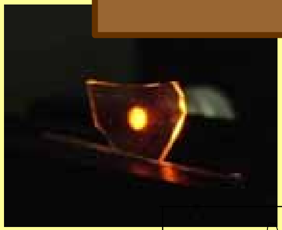
Rare-earth in Glasses

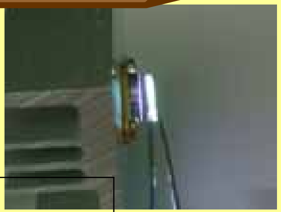
Spectral Hole-burning

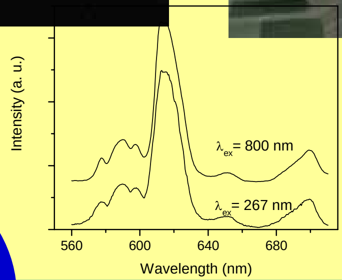
PSHB spectrum in Eu^{3+}-doped glass



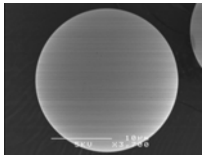
Fluorescence



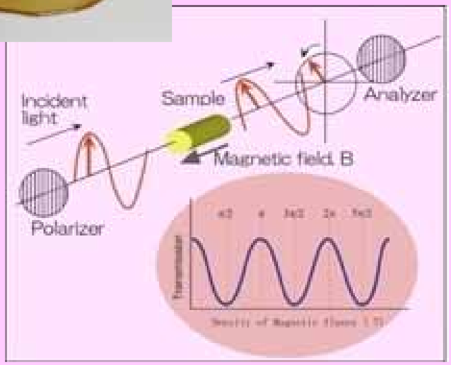




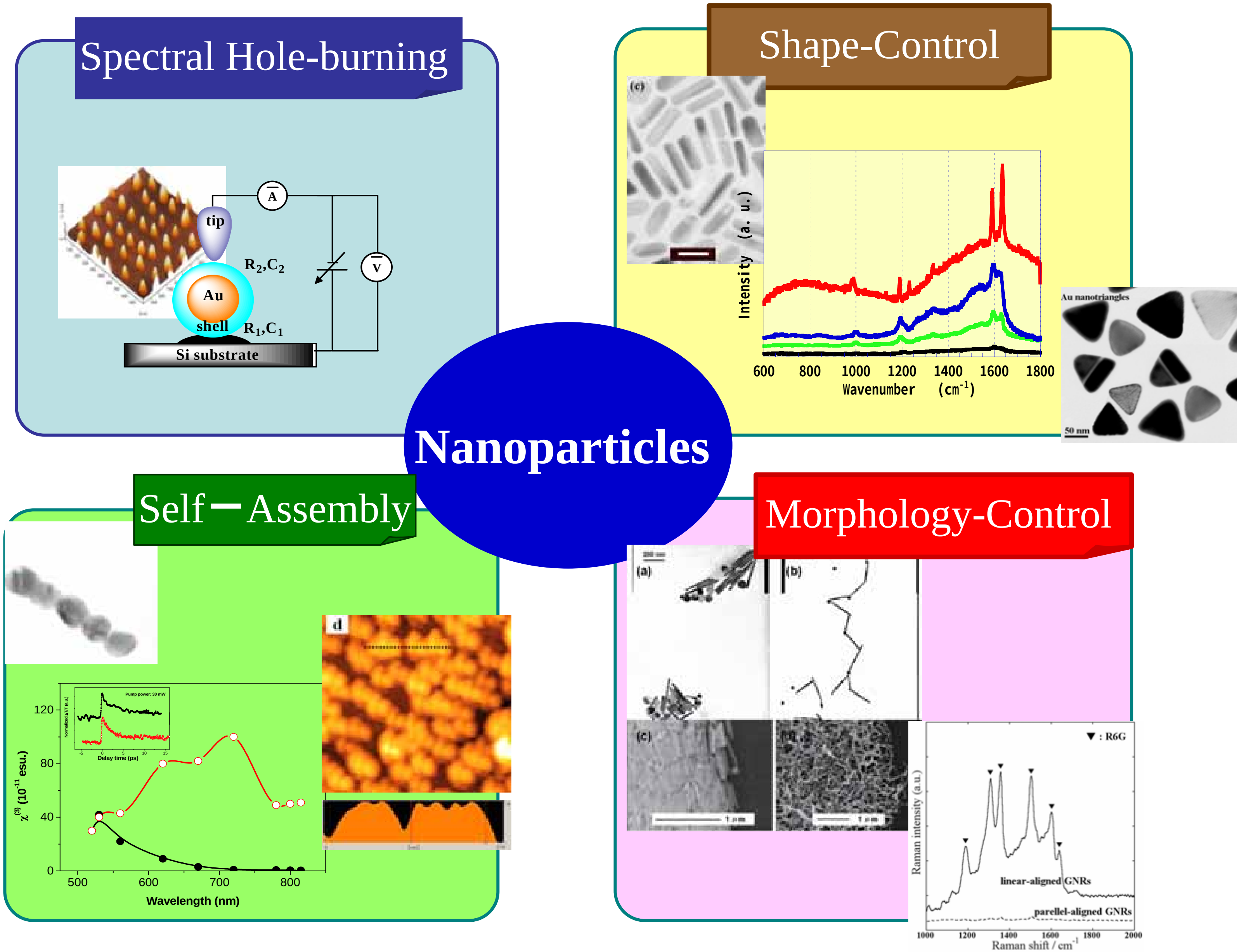
Laser



Faraday rotation



Self-Assembling of Nano-Particles and Nonlinear Optics



Proton conduction in glass and its application to fuel cell

- **Introduction**

  Possibility of fast proton conduction in the glass

- **Sol-gel method for preparation of proton conducting glasses**

  Mechanism of proton conduction in porous glass

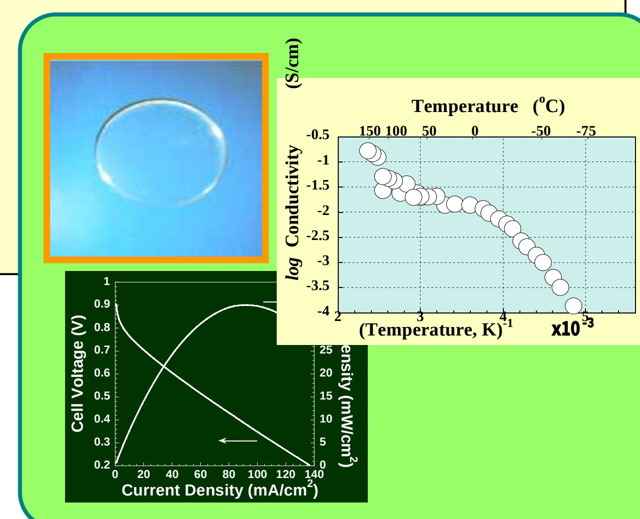
  Glasses and films exhibiting high proton conductivities at

  150ºC ~ -100ºC

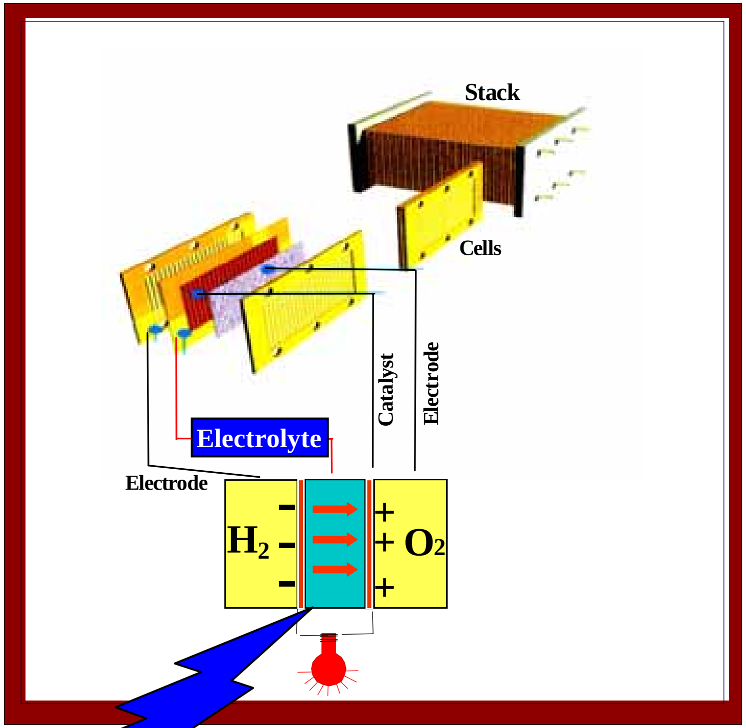
- **Applications**

  Electrolytes for gas sensor and fuel cell

- **Conclusions**



High proton conducting glasses for the fuel cell electrolyte



Anode

$H_2 \longrightarrow 2H^+ + 2e^-$

Cathode

$2H^+ + 1/2O_2 + 2e^- \longrightarrow H_2O$

Total

$H_2 + 1/2O_2 \longrightarrow H_2O$

High efficiency, Clean energy

Electrolyte

Proton conducting membrane

Perfluorosulfonate ionomers (Nafion)

High proton conductivity at around room temperature

Degradation in thermal and chemical attacks

⟹

Inorganic Sol-gel-derived Glass

High proton conductivity at temperatures of 150°C to -30°C

High stability against the thermal and chemical attacks

Fast proton conducting-glasses prepared by the sol-gel process

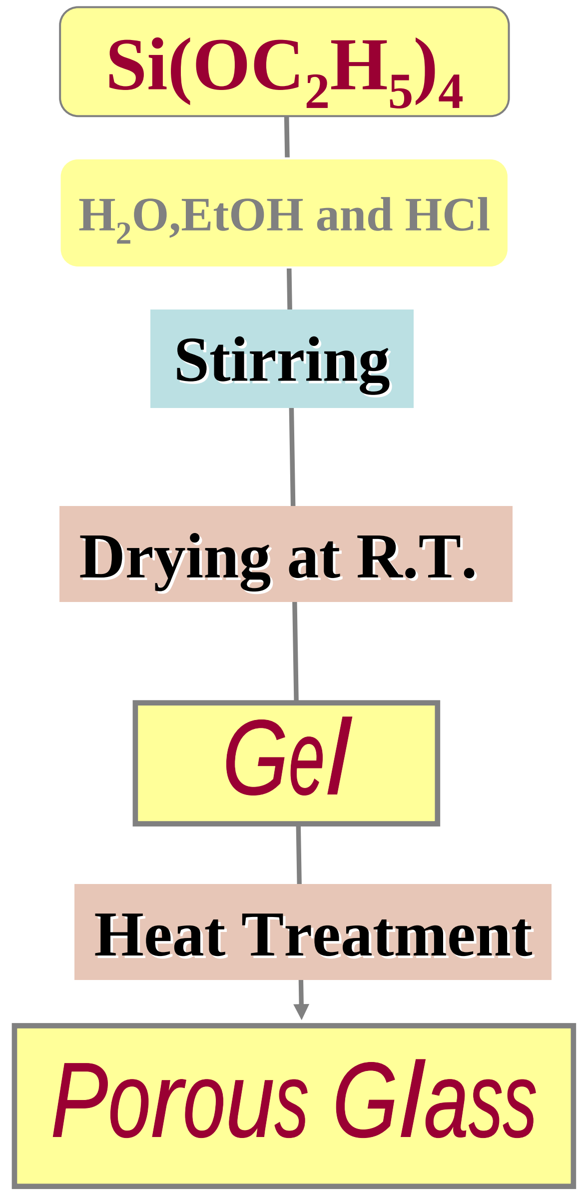
- Mechanism of proton conduction in the sol-gel-derived porous glasses.

- Effect of pore structure on the proton conduction.

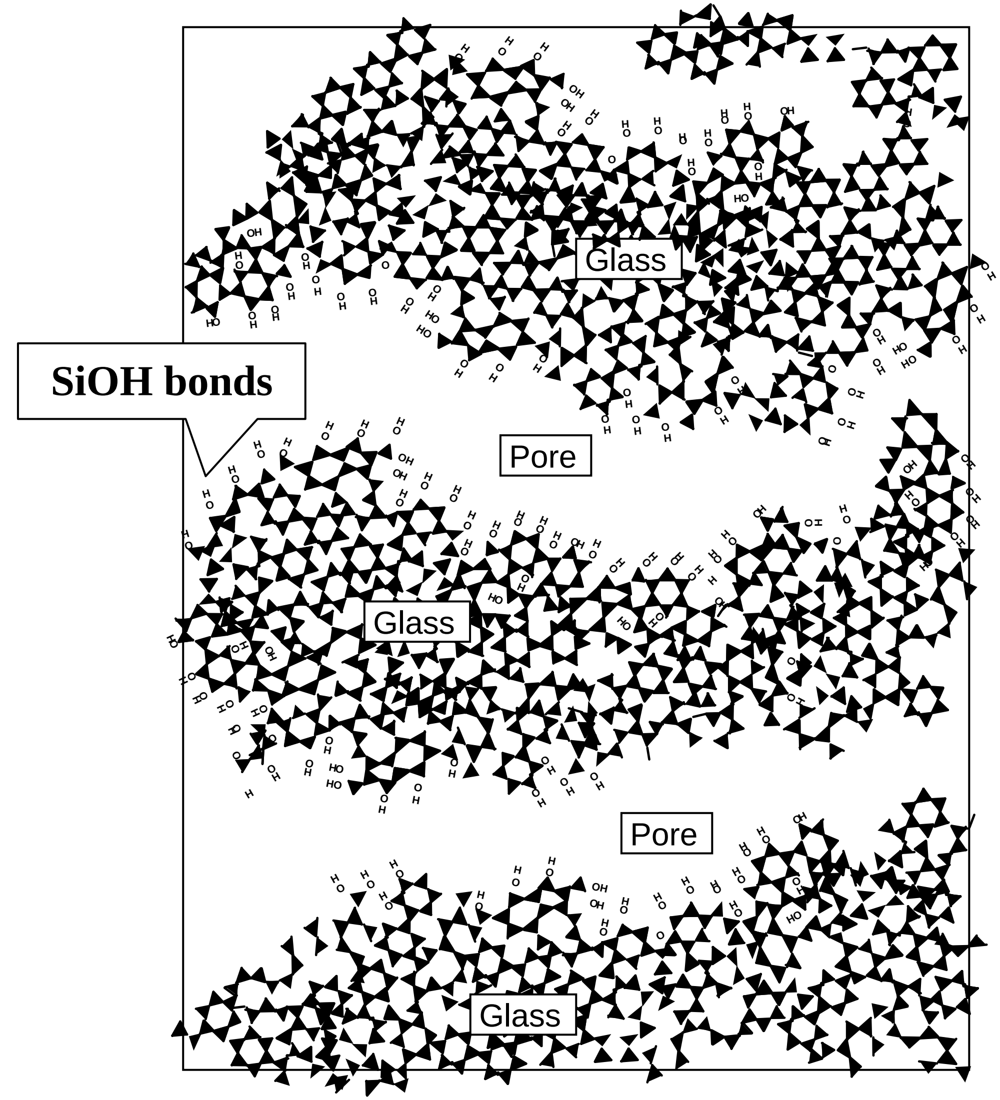
- Preparation of glass films with ordered pore structure.

- Application to the gas sensor and fuel cell.

Sample Preparation

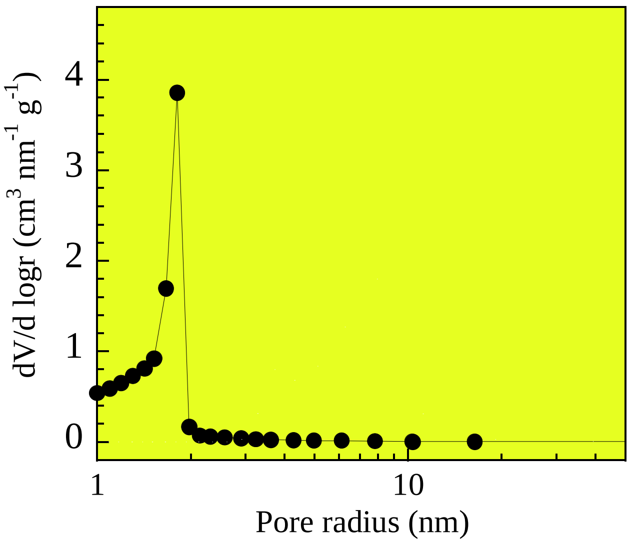


Porous structure of the sol-gel-derived glasses

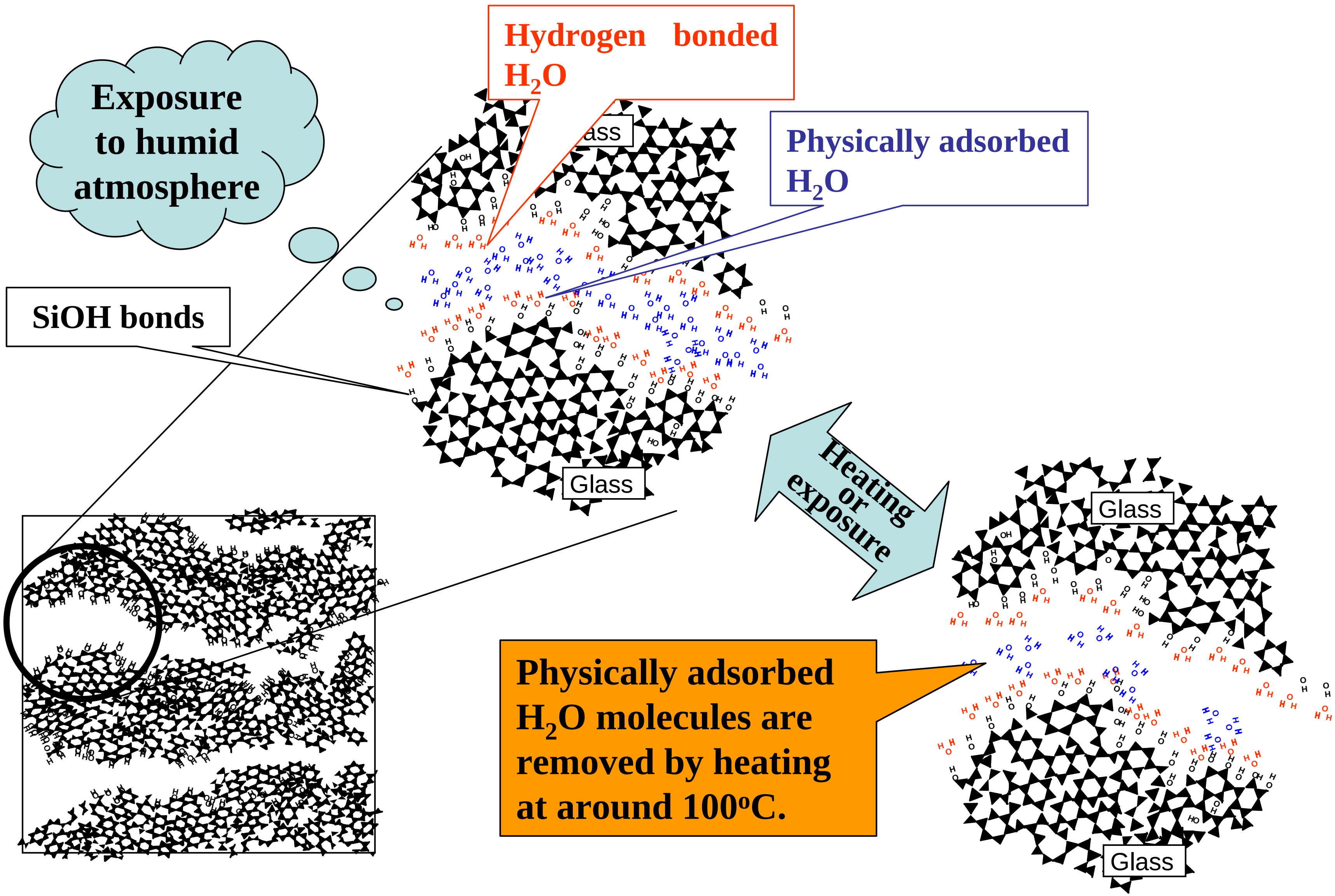


Porous properties of the glass

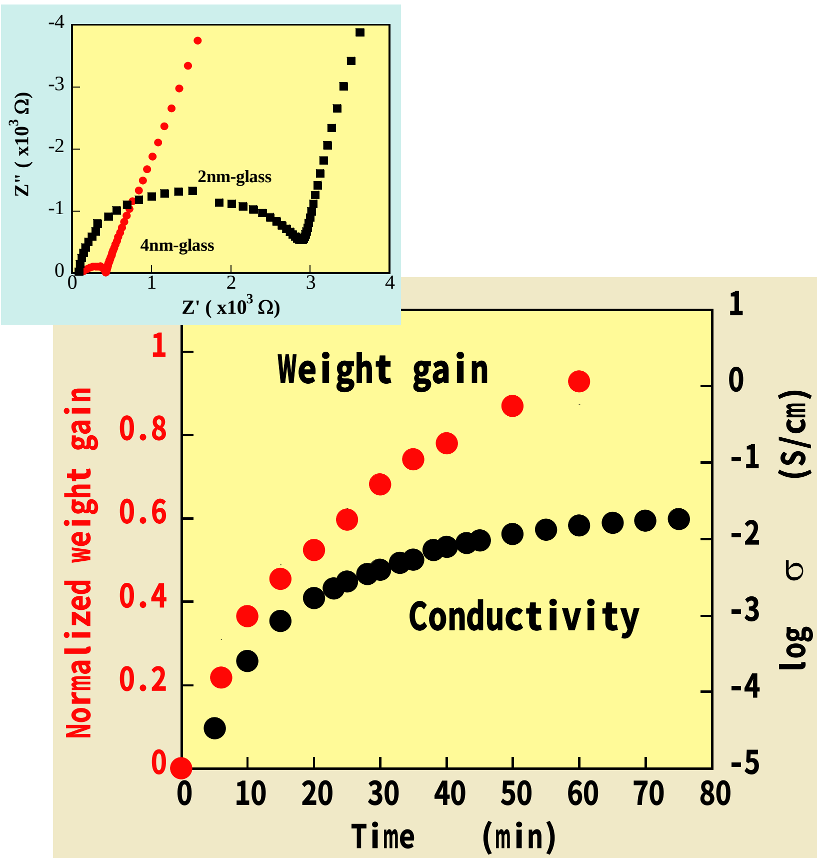
Surface Area
up to ~1000m²/g
Pore volume
0.1 ~ 0.5 cm³/g
Pore size
> 1 nm

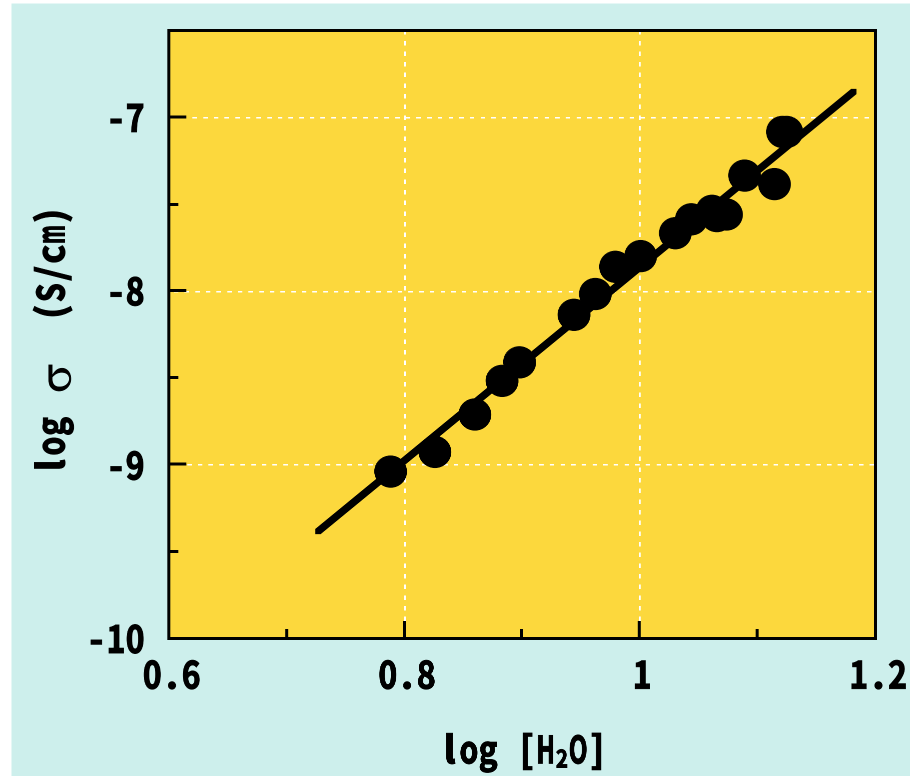


Water molecules absorbed in the porous glasses



Effect of the physically bonded H_2O molecules on the conductivity

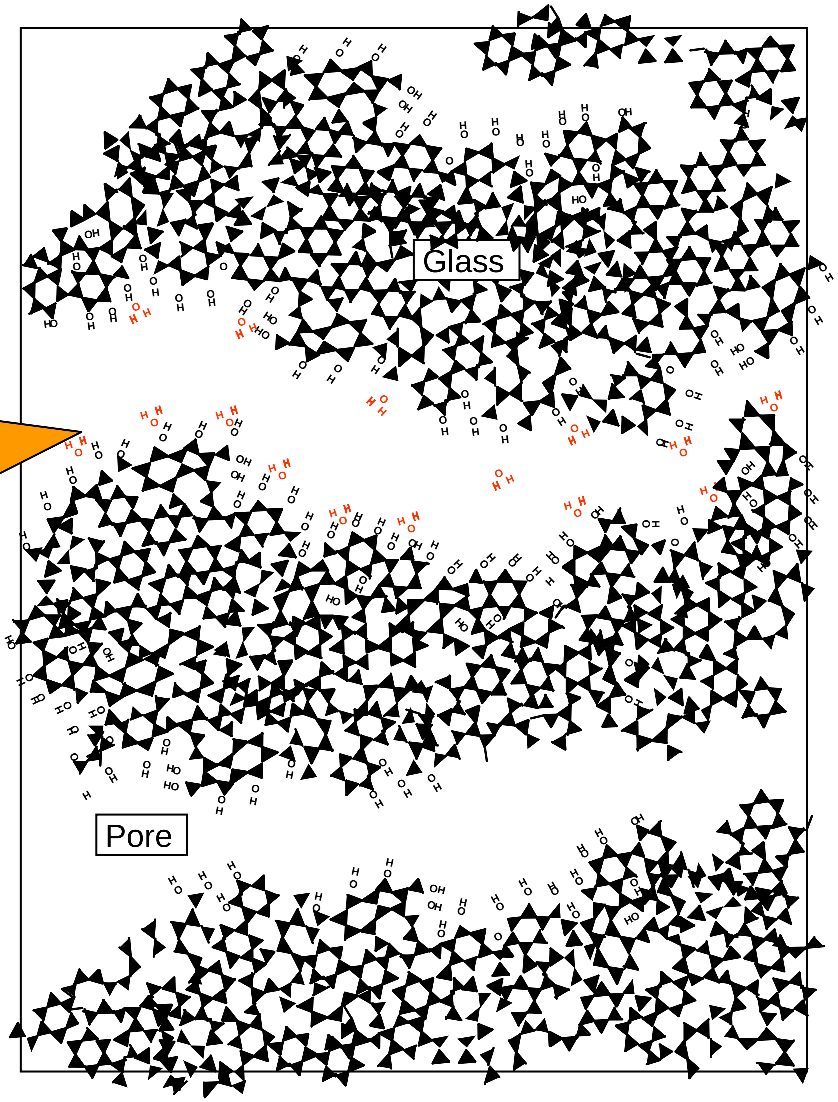




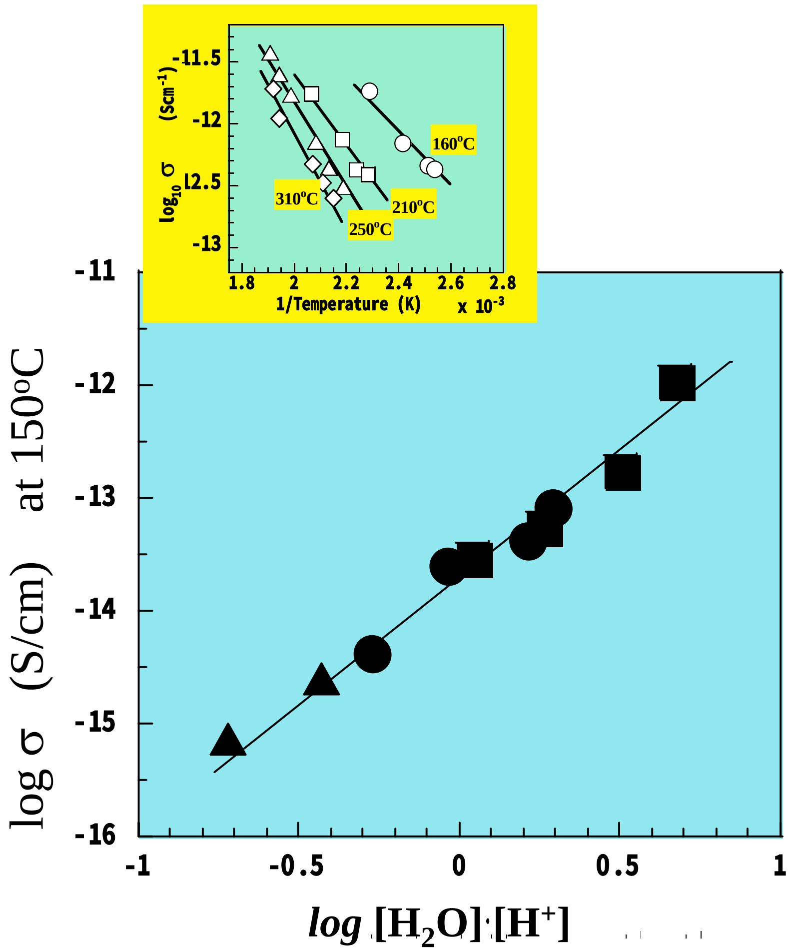
$$\log \sigma = K \log [H_2O]$$

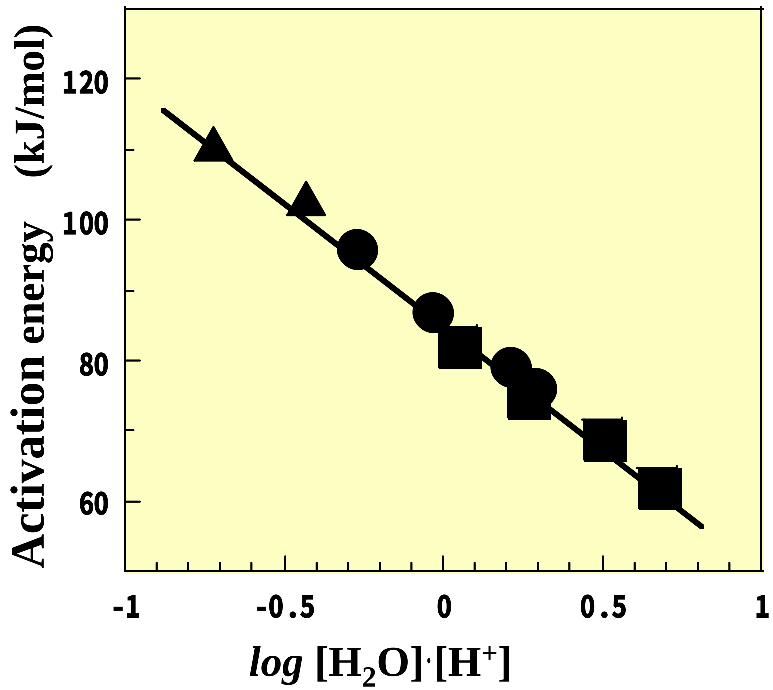
Controlling the amount of the chemically bonded H_2O molecules

Chemically bonded H_2O molecules are removed by heating at around 200°C.



Effect of the chemically bonded H_2O molecules on the conductivity and its activation energy

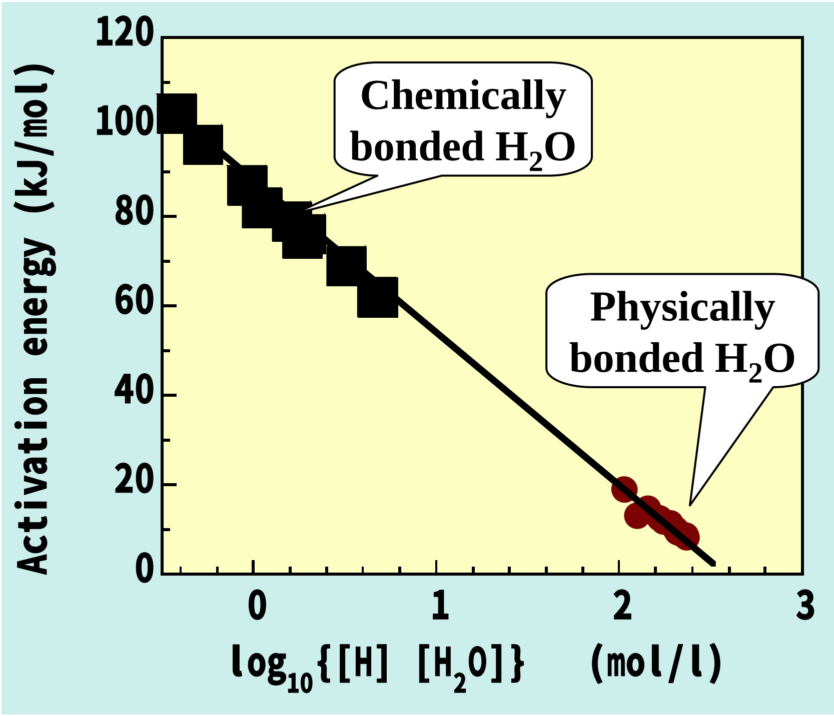




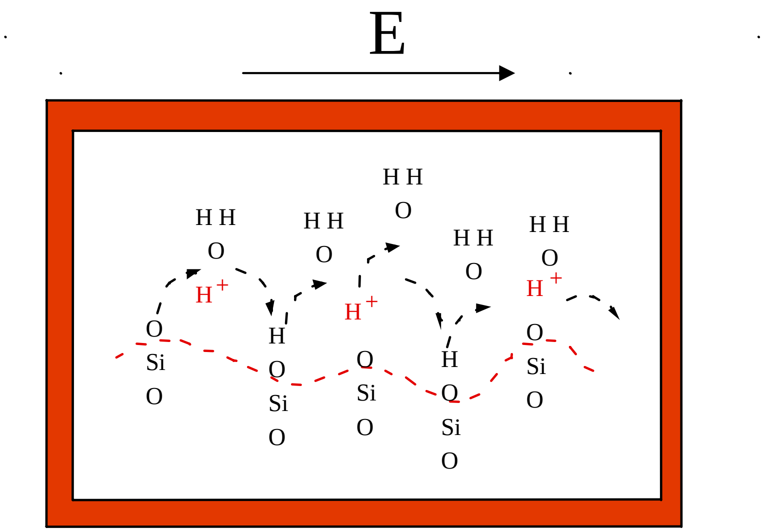
$$\log \sigma = k \log [H_2O]\cdot[H^+]$$

$$E = k \log [H_2O]\cdot[H^+]$$

Proton conduction in the porous glass



Conduction process of proton through the porous glass

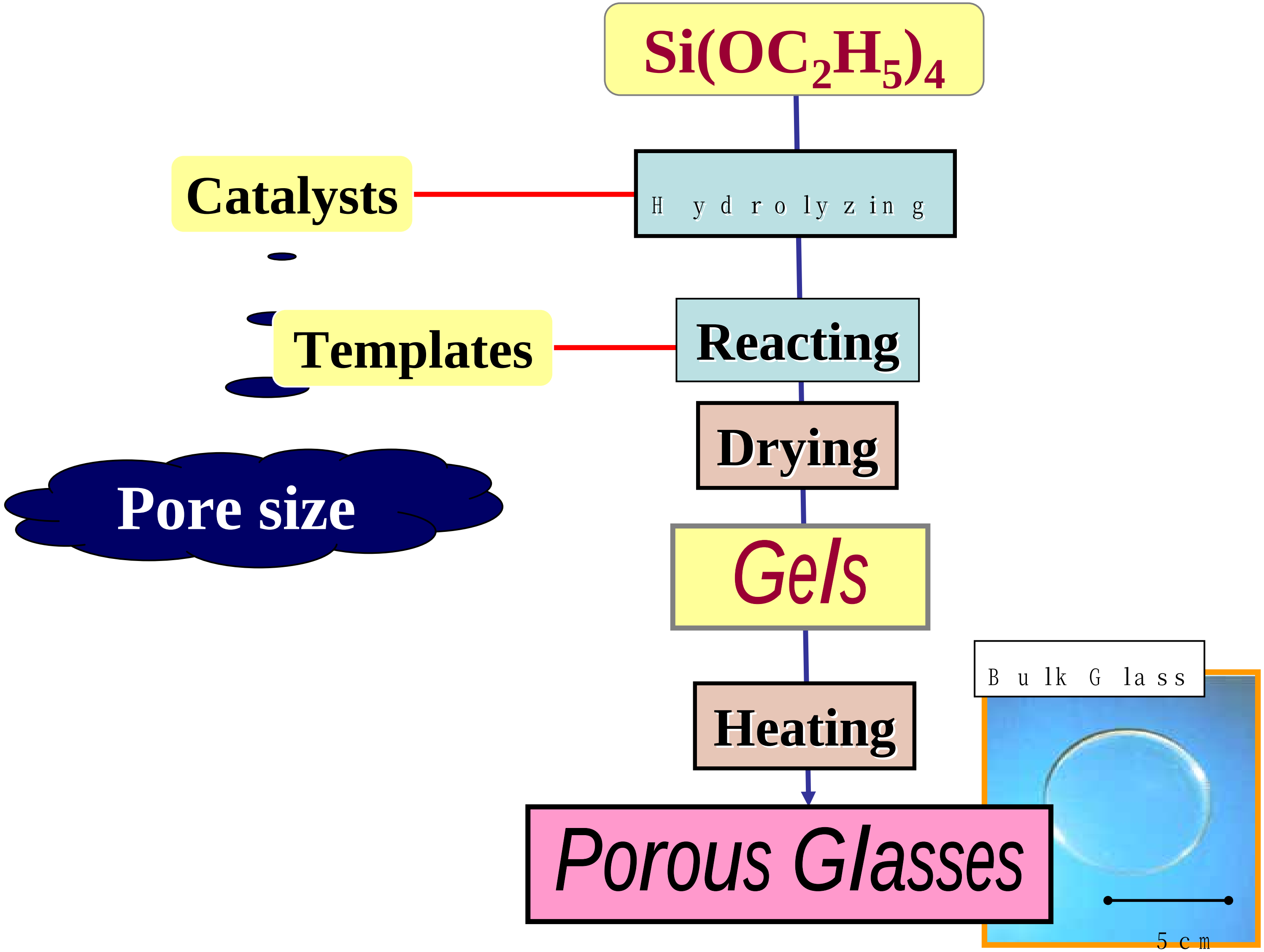


Proton conduction is controlled by the proton dissociation from the SiOH bond and the proton hopping between SiOH and H_2O.

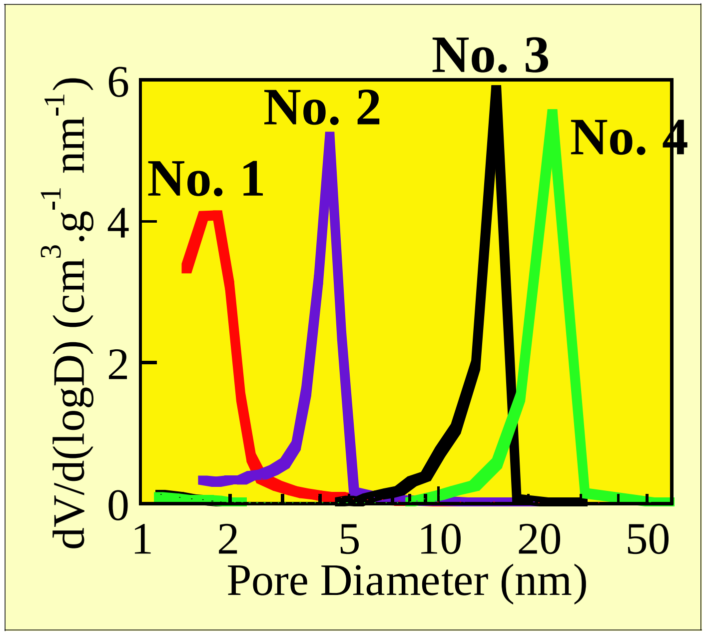
Fast proton conducting-glasses prepared by the sol-gel process

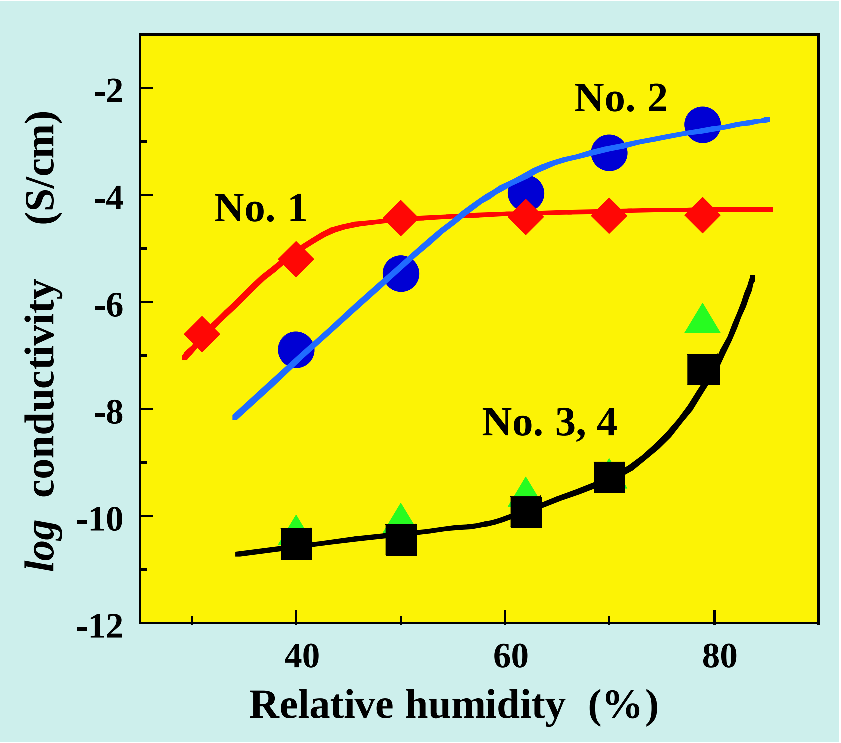
- Mechanism of proton conduction in the sol-gel-derived porous glasses.
- Effect of pore structure on the proton conduction.
- Preparation of glass films with ordered pore structure.
- Application to the gas sensor and fuel cell.

Preparation of glasses with different pore size

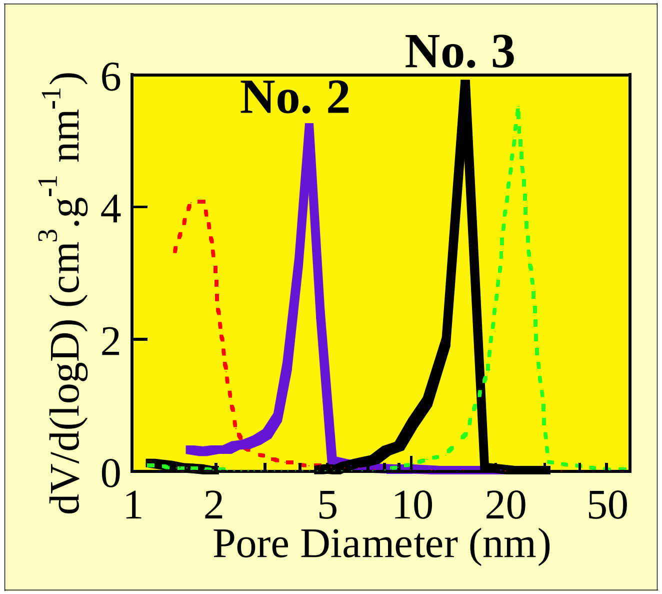


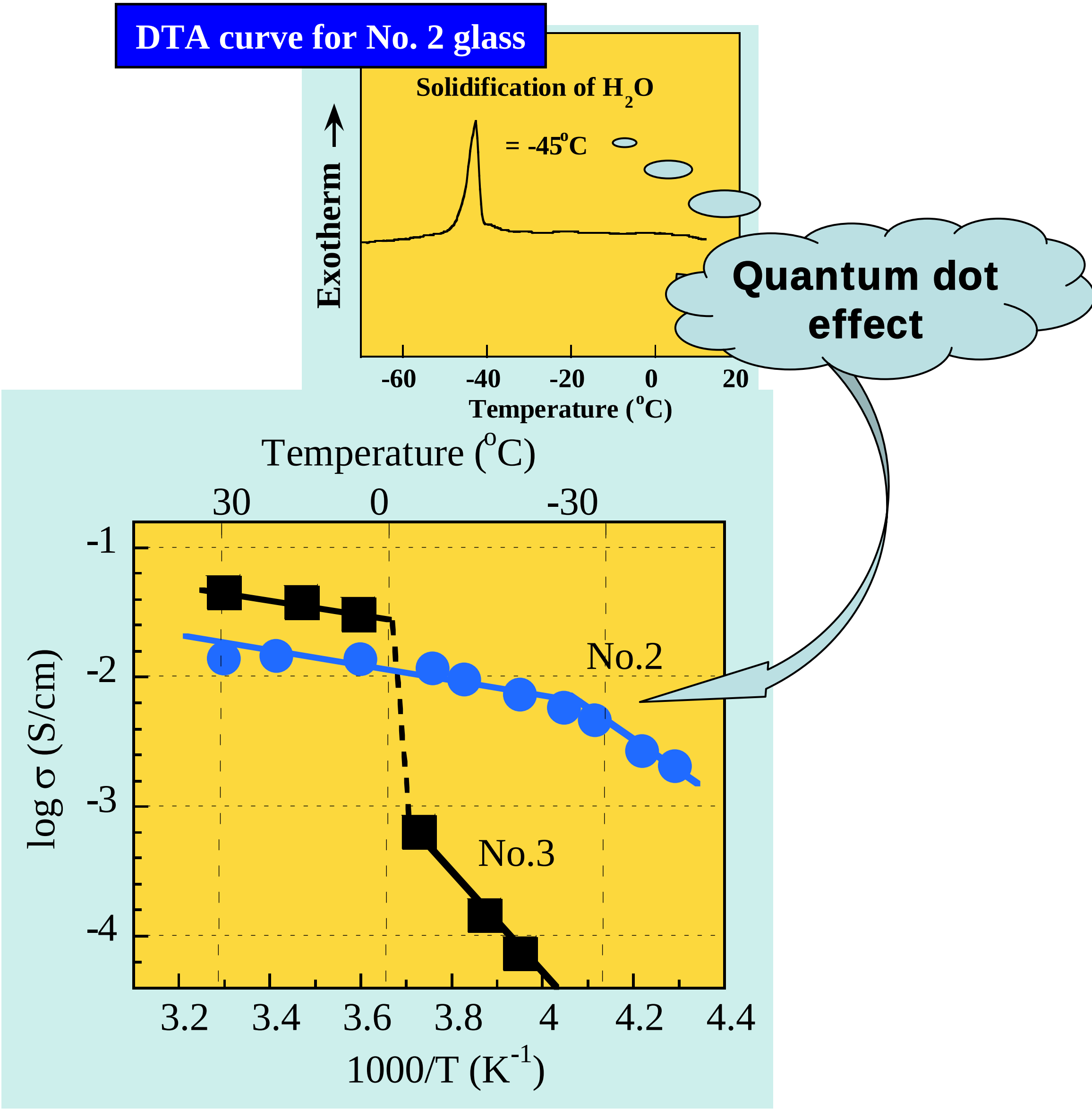
Pore size distribution and its effect on the conductivity



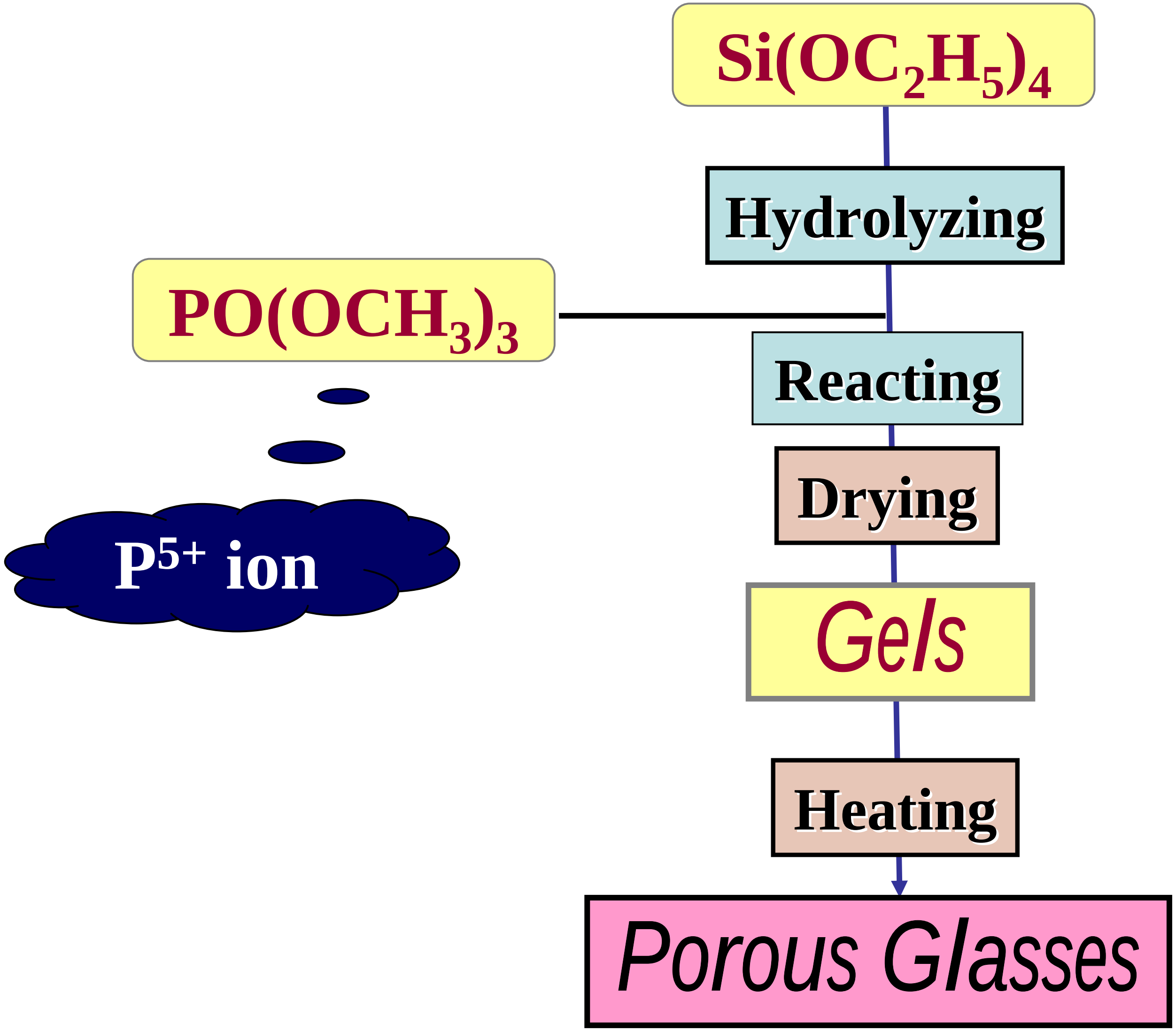


Effect of the pore size on the proton conductivity





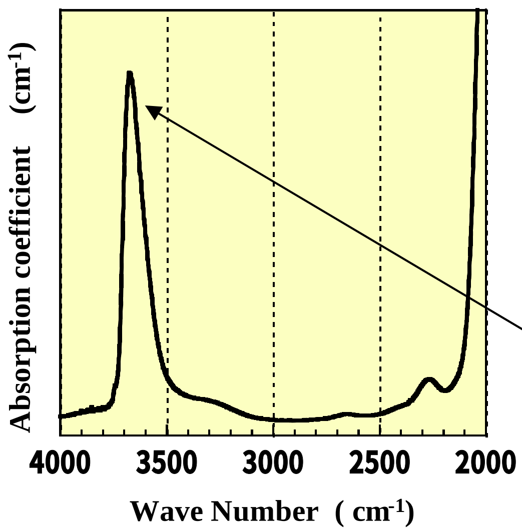
Effect of P_2O_5 on proton conductivity



FT-IR

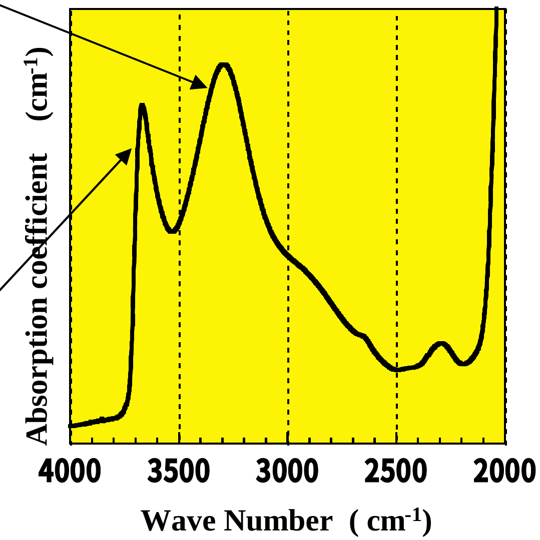
Glass Composition

SiO_2 glass



H
P -OH ········ O
H

P_2O_5-SiO_2 glass



H
Si -OH ········ O
H

Dissociation energy for proton;
SiOH > POH

→

High proton conductivity can be expected for POH bonds.

Dependence of Conductivity on Temperature

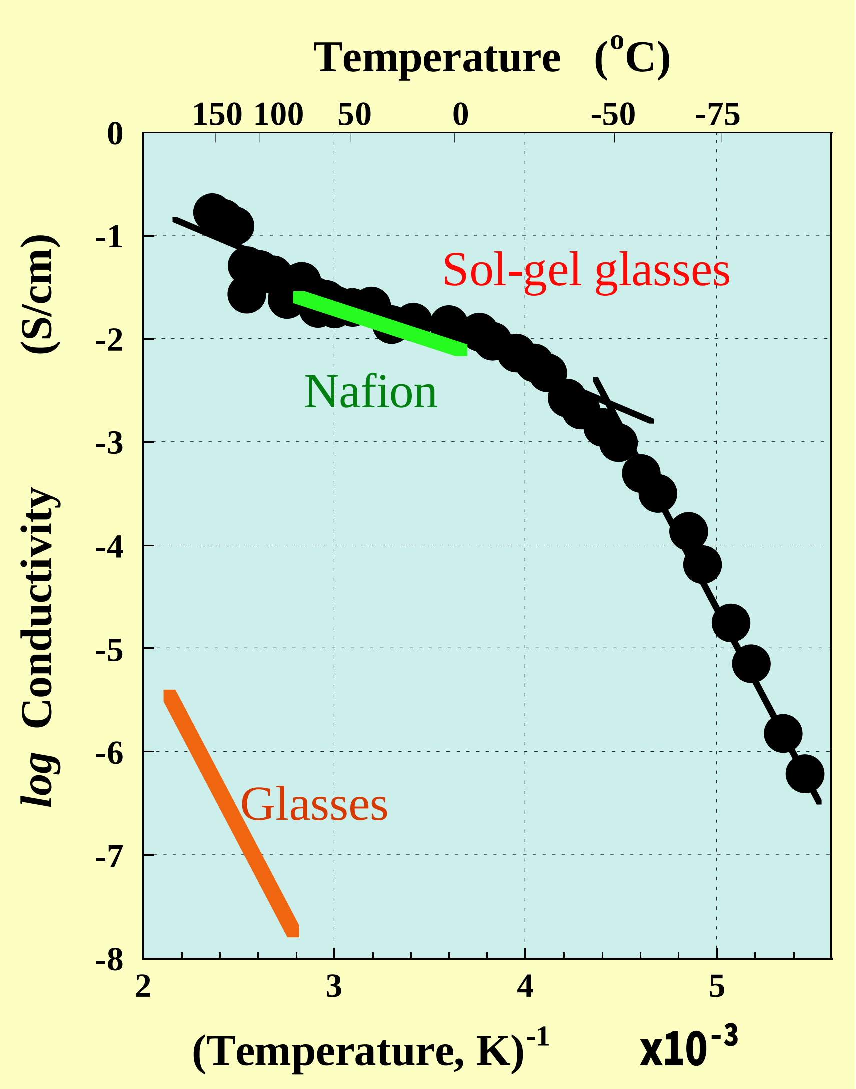
- **Proton conduction mechanism**

  proton dissociation from the SiOH bond and the proton hopping between SiOH and H_2O.

- **High proton conductivity in wide temperature range**

  -30ºC to 150ºC

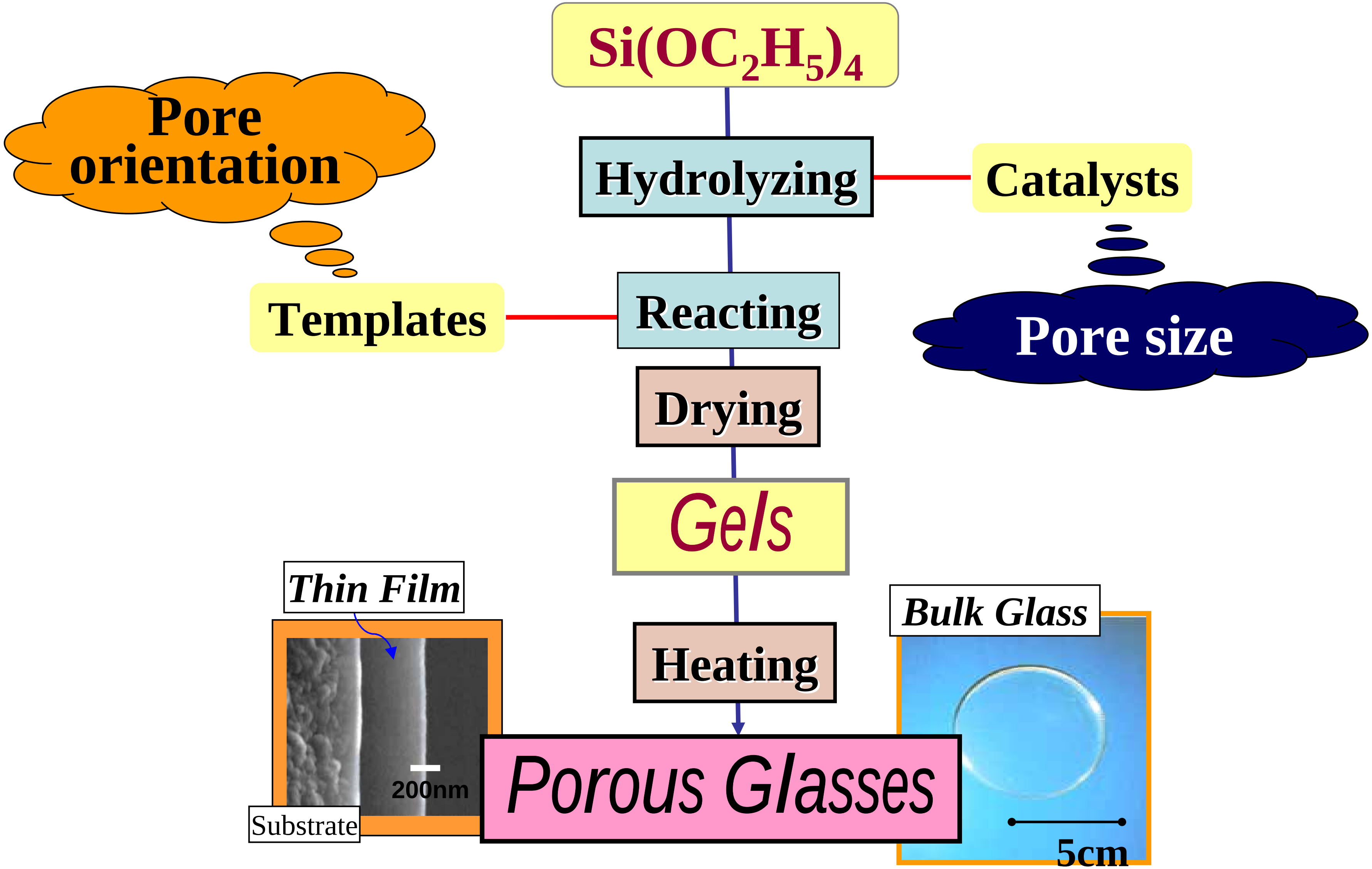
  (ex. 170 mS/cm at 150ºC)



Fast proton conducting-glasses prepared by the sol-gel process

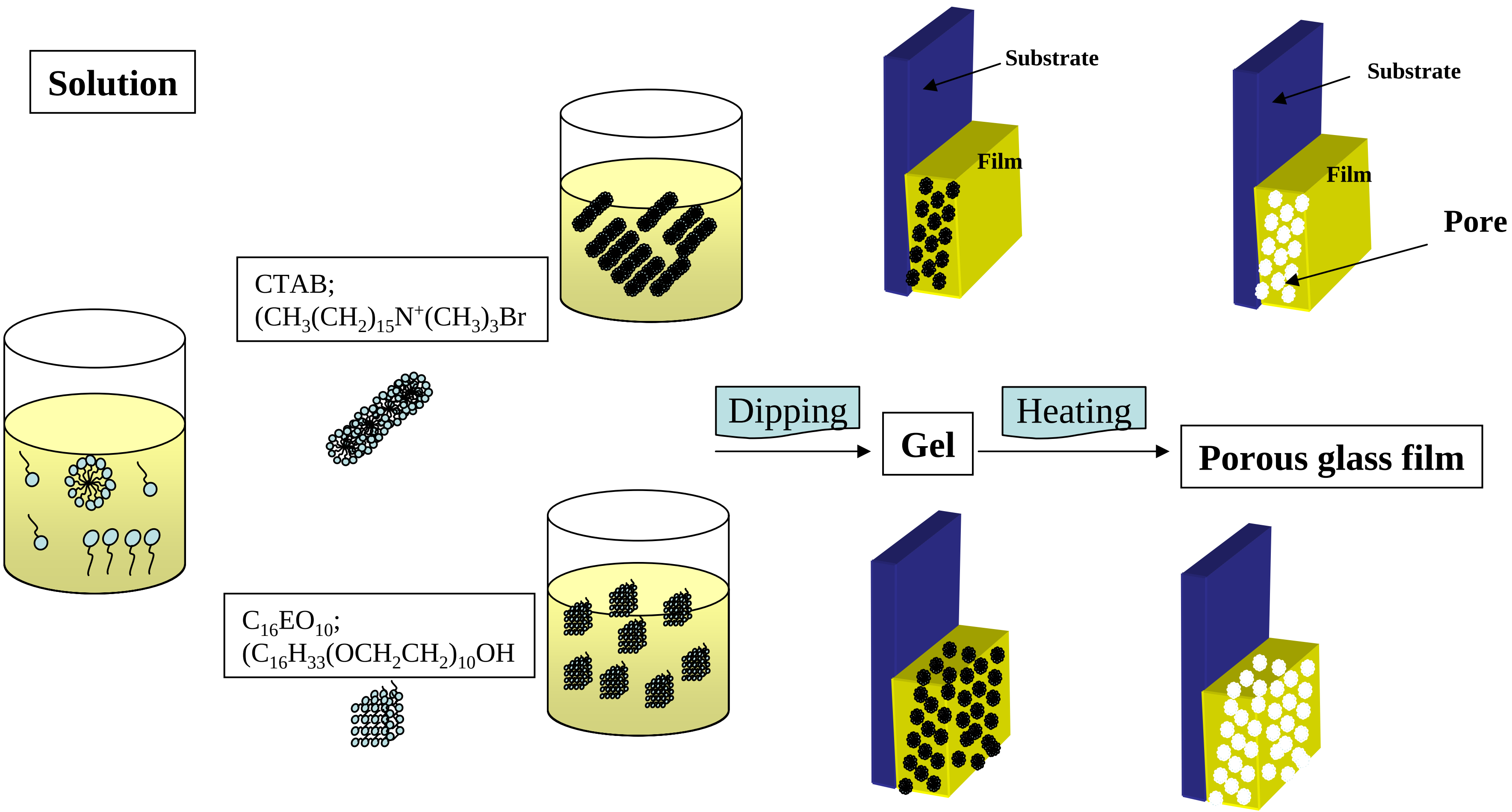
- Mechanism of proton conduction in the sol-gel-derived porous glasses.
- Effect of pore structure on the proton conduction.
- Preparation of glass films with ordered pore structure.
- Application to the gas sensor and fuel cell.

Preparation of pore-oriented glass films

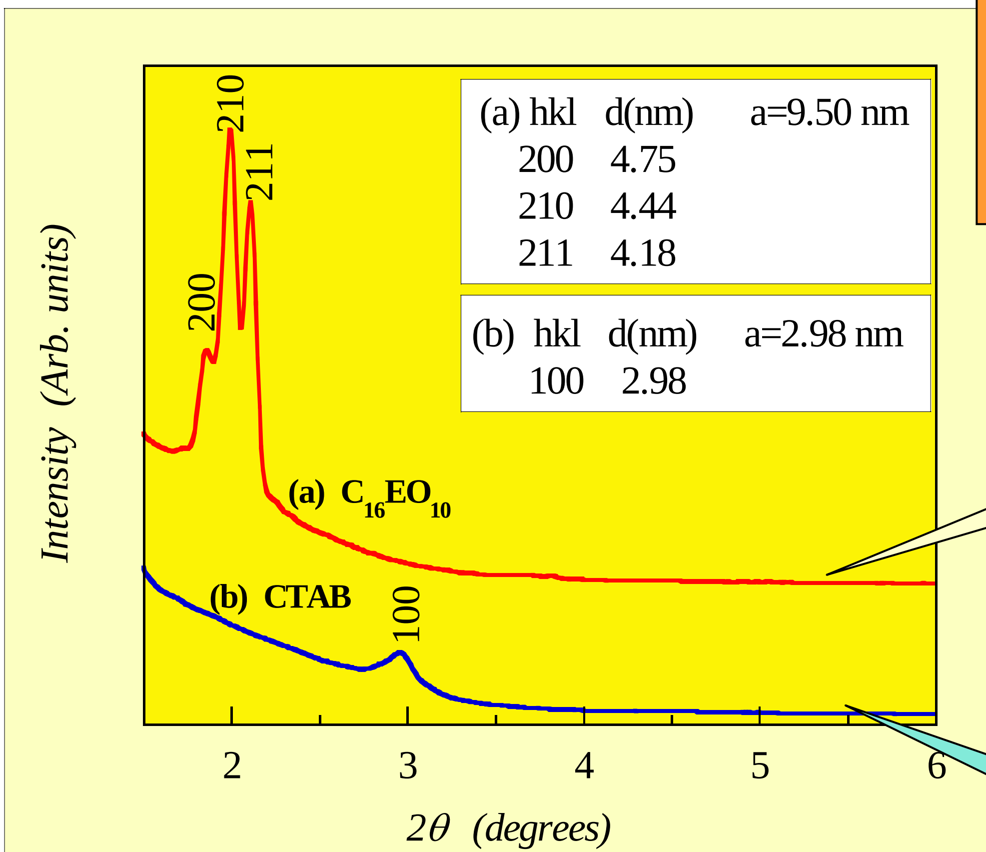


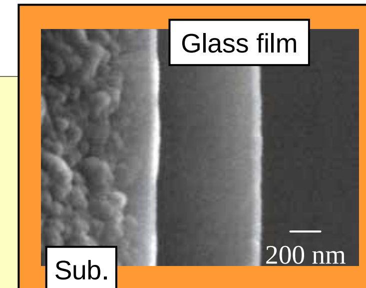
Pore-oriented glass films by self-assembling method

Preparation of glass film by self-assembling method using templates



Self-assembled pore-oriented glass films

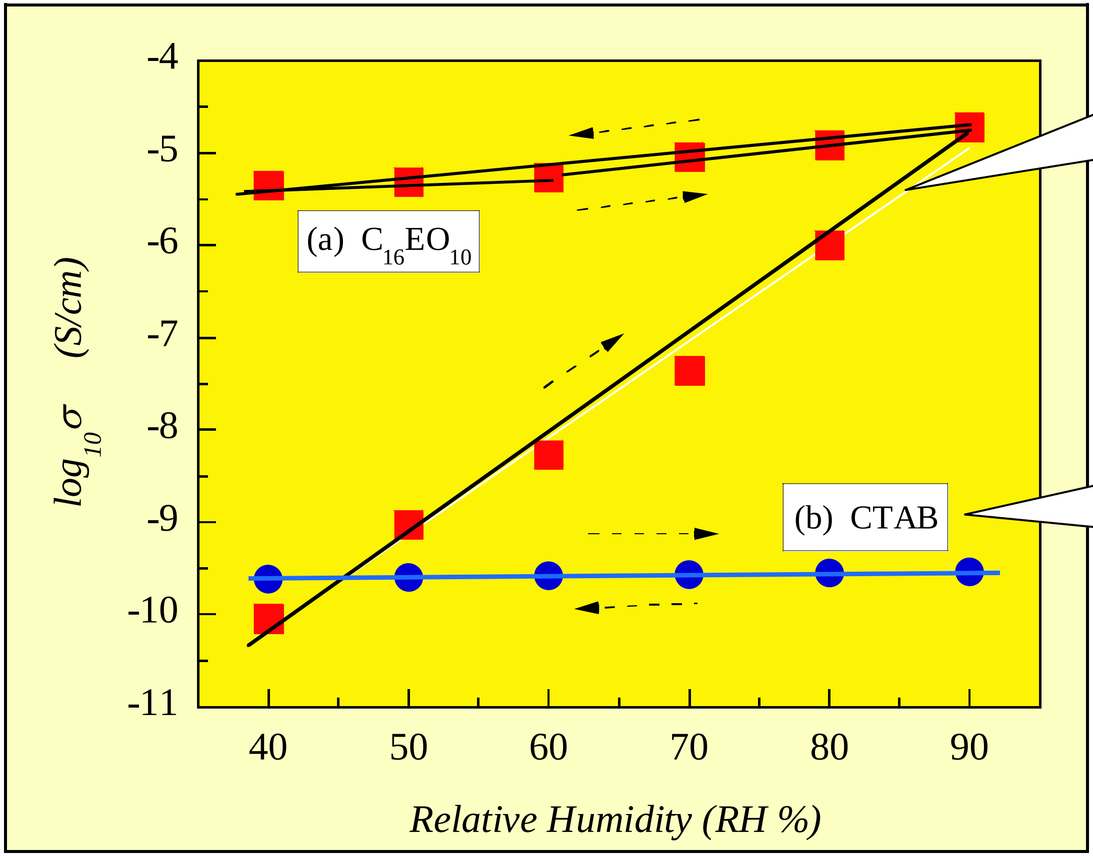


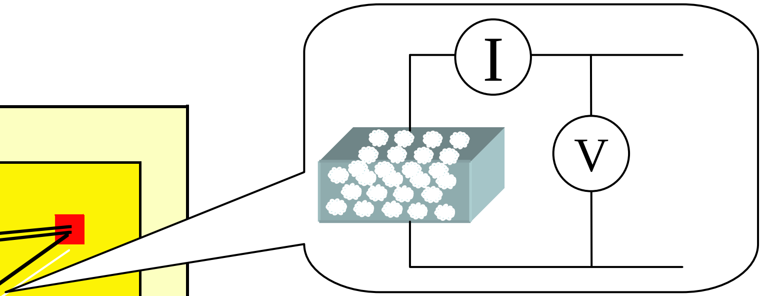


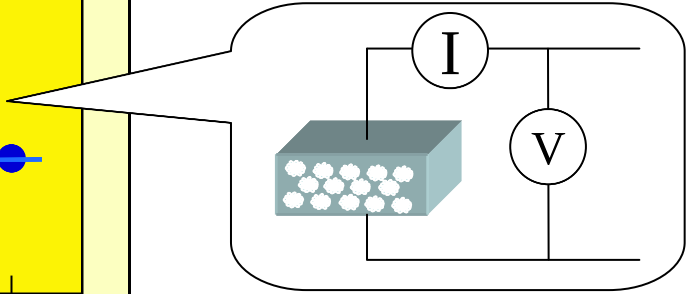
Cubic

Hexagonal

Conductivities of pore-oriented glass films







Fast proton conducting-glasses prepared by the sol-gel process

- Mechanism of proton conduction in the sol-gel-derived porous glasses.
- Effect of pore structure on the proton conduction.
- Preparation of glass films with ordered pore structure.
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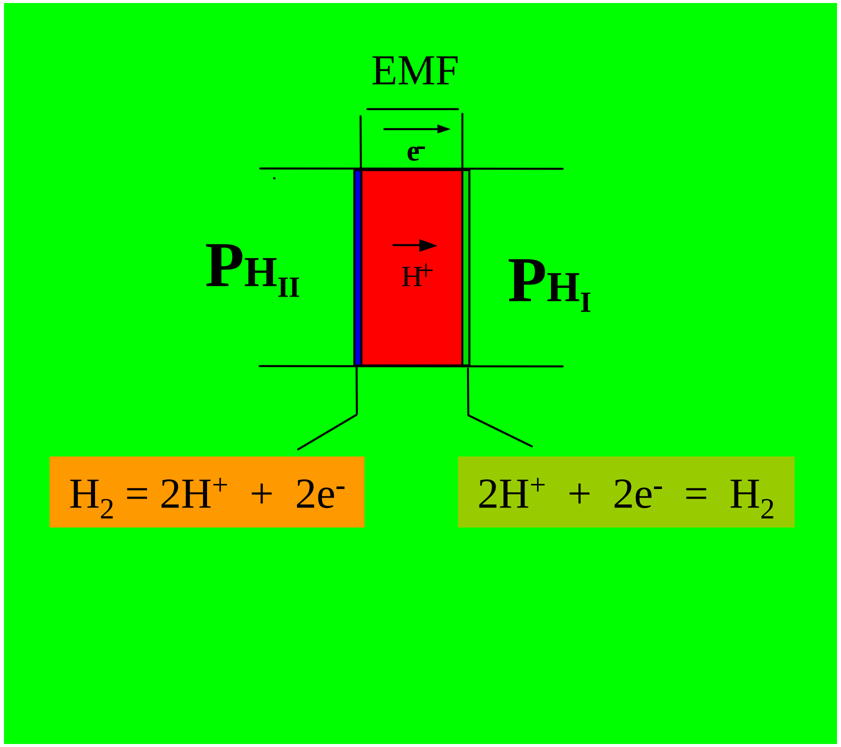
Application of proton conducting glasses

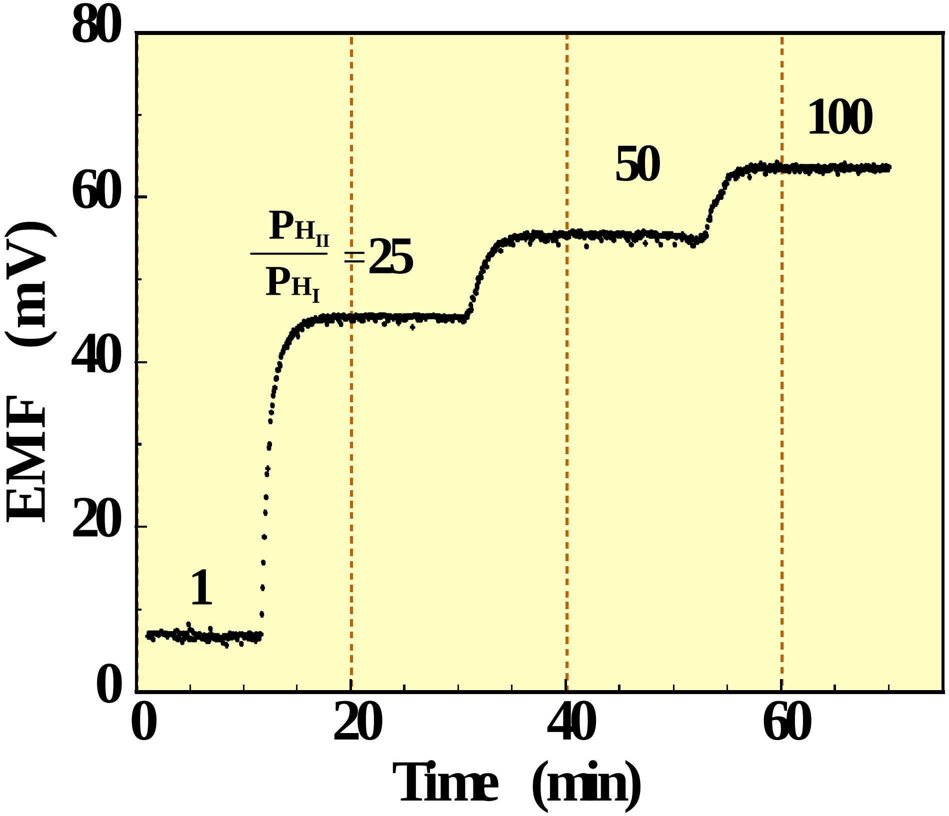
Sensors

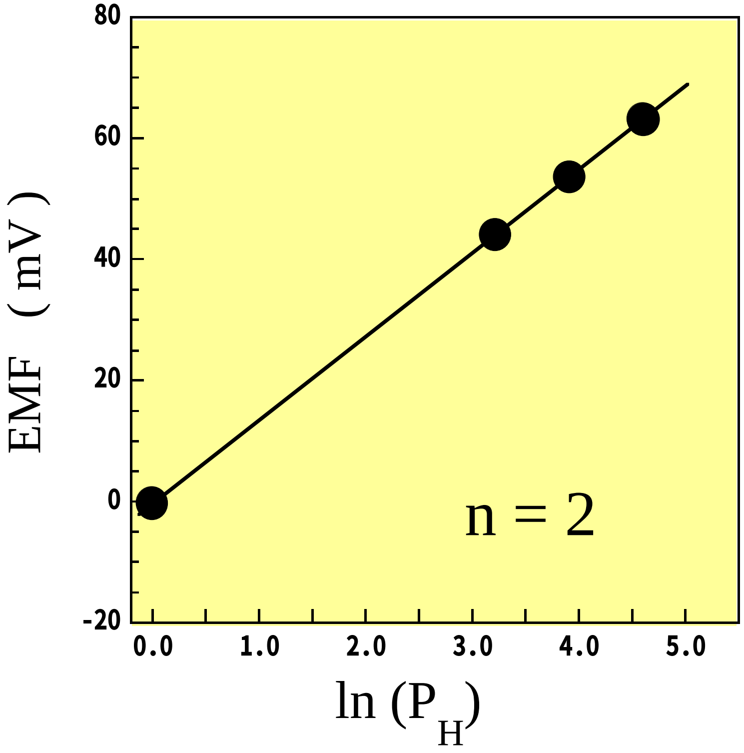
Hydrogen, Humidity



$$EMF = \frac{RT}{nF} \, ln \frac{P_{H_{II}}}{P_{H_{I}}}$$

Responsibility to H_2 gas

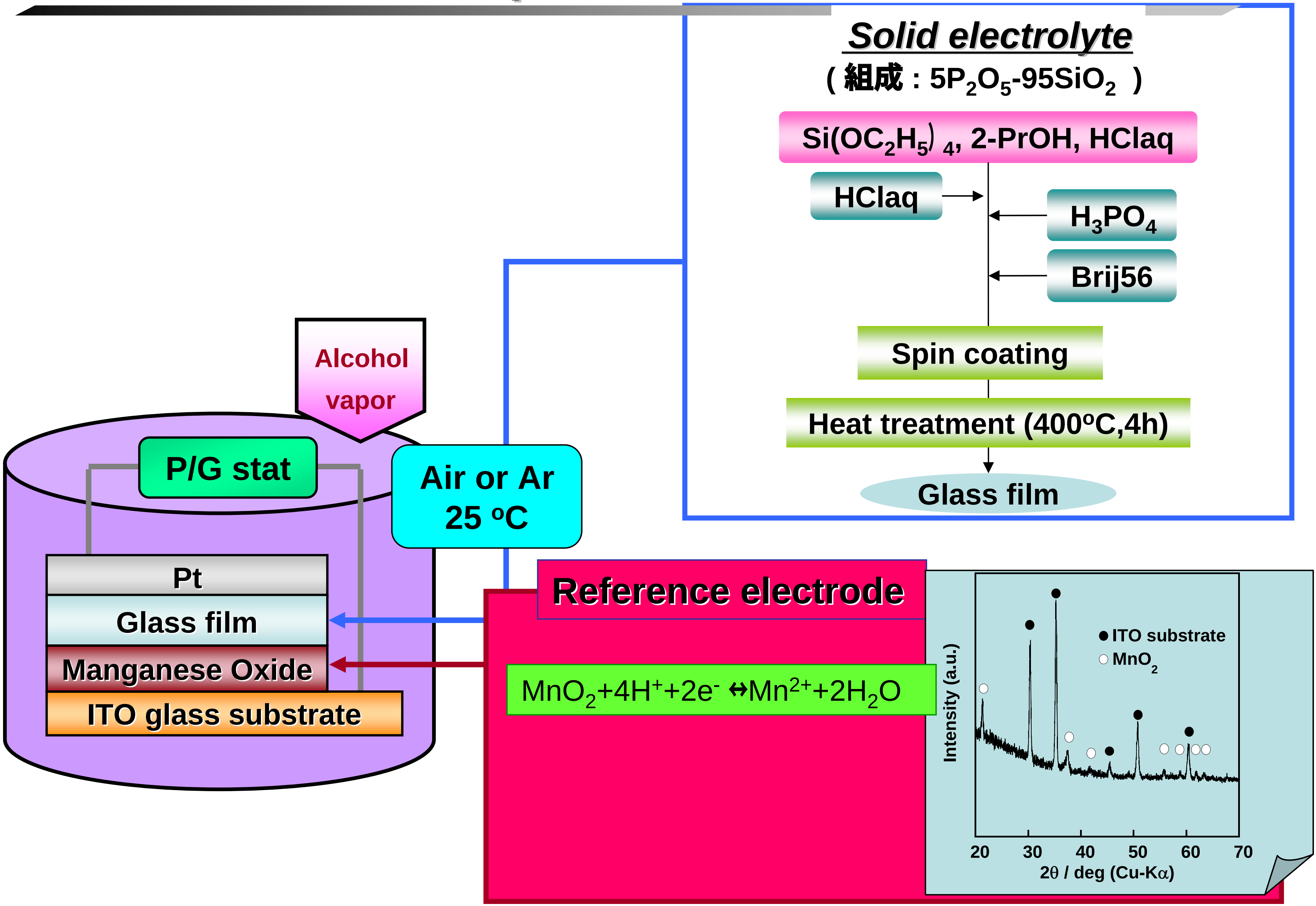




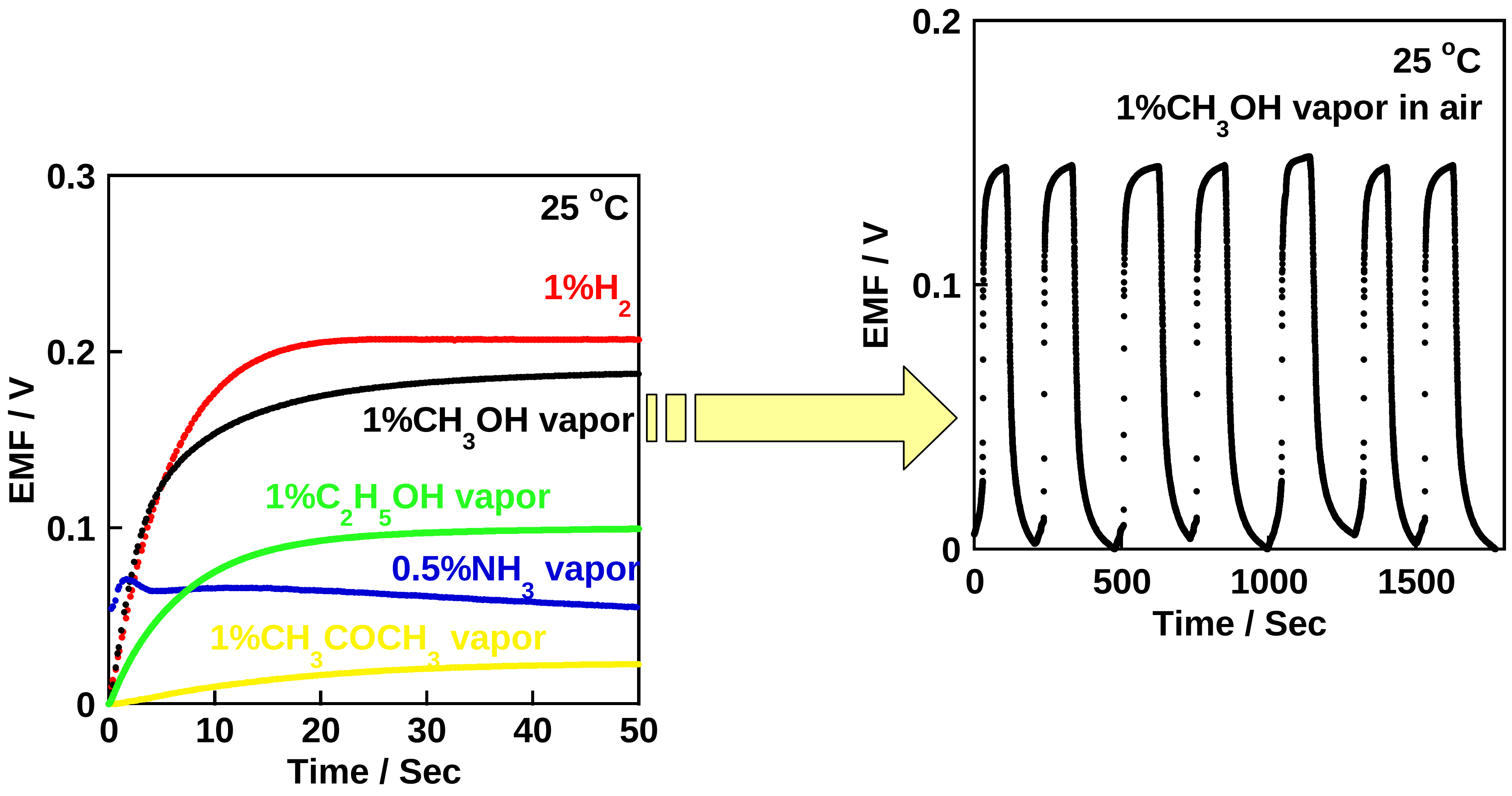
$$EMF = (RT/nF)\, ln(P_H)$$

$H_2 = 2H^+ + 2e^-$

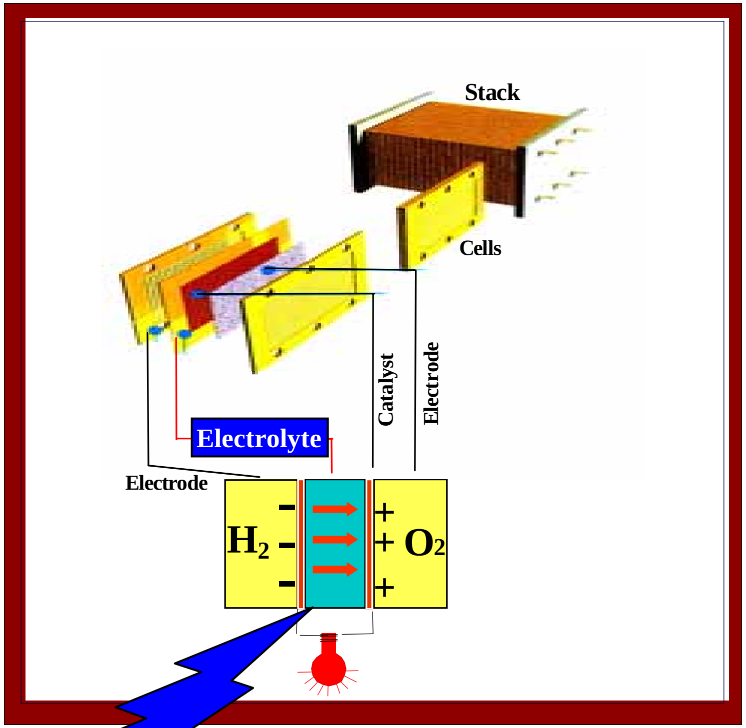
Gas sensors ~ Preparation of thin films ~



Gas sennsing



High proton conducting glasses for the fuel cell electrolyte



Anode

$$H_2 \longrightarrow 2H^+ + 2e^-$$

Cathode

$$2H^+ + 1/2O_2 + 2e^- \longrightarrow H_2O$$

Total

$$H_2 + 1/2O_2 \longrightarrow H_2O$$

High efficiency, Clean energy

Electrolyte

Proton conducting membrane

Perfluorosulfonate ionomers (Nafion)

High proton conductivity at around room temperature

Degradation in thermal and chemical attacks

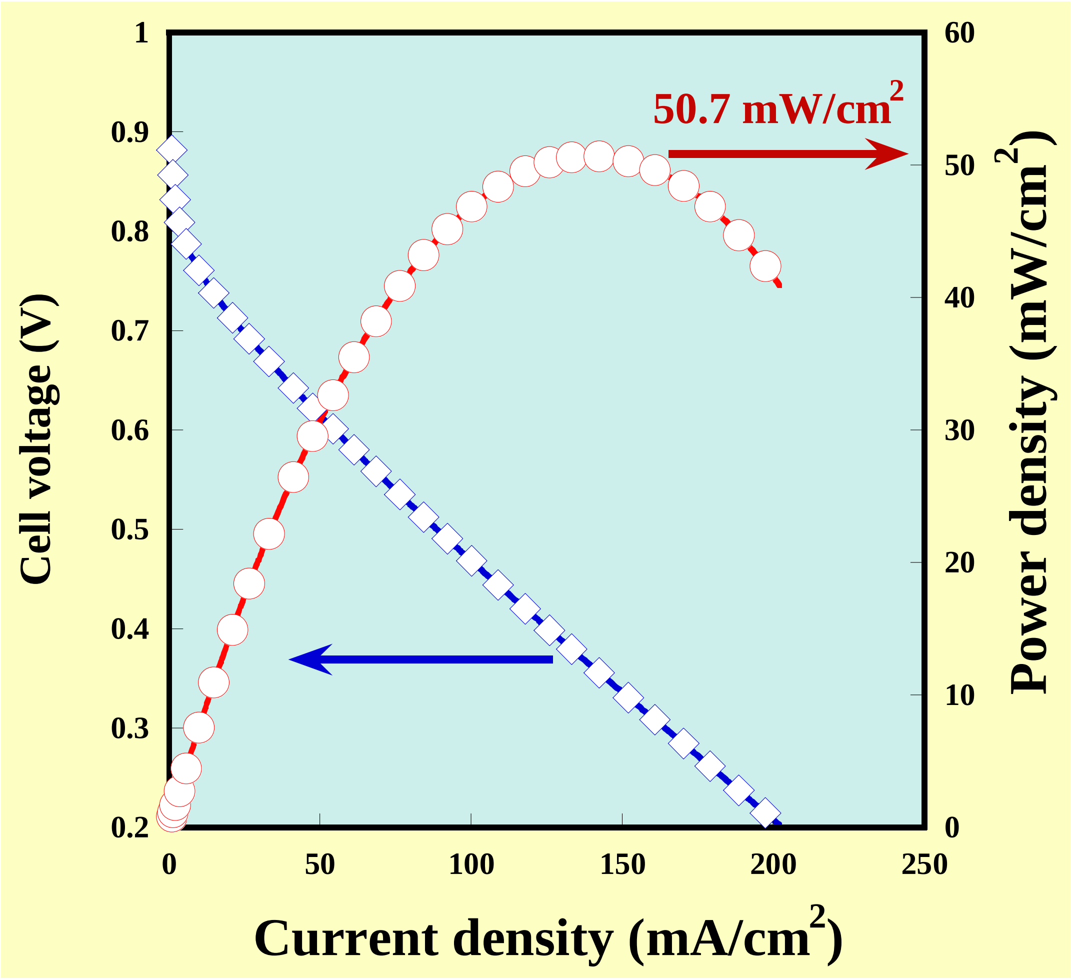
⟹

Inorganic Sol-gel-derived Glass

High proton conductivity at temperatures of 150°C to -30°C

High stability against the thermal and chemical attacks

Fuel Cell



50.7 mW/cm2
Cell voltage (V)
Power density (mW/cm2)
Current density (mA/cm2)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
60
50
40
30
20
10
0
0
50
100
150
200
250

Conclusions

- Fast proton-conducting porous glass
  - + Preparation by the sol-gel method
    - Porous glass with large surface area and small-sized pores
  - + Proton conduction process
    - Dissociation of the protons and their hopping between water molecules and hydroxyl groups
- High proton conductivities
  - +In wide temperature range from -30ºC to 150ºC
    - ex. 170 mS/cm at 150ºC
- Glass films having high-ordered pore structure
- Possible application as the electrolyte
  - + Sensor and Fuel cell

Thank you