Lecture 4, Part 1: Proton conduction in glass sand its application to fuel cell - Proton conduction

Masayuki Nogami
Nagoya Institute of Technology, Japan

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Proton conduction in glass and its application to fuel cell

Masayuki NOGAMI

Department of Materials Science and Engineering,
Graduate School of Engineering,
Nagoya Institute of Technology

Email: nogami@nitech.ac.jp

Home Page: http://nitzy.mse.nitech.ac.jp/~nogamilab/index.html
- New optical glasses
- Fast proton conducting glasses and their application to fuel cell
- Self-assembling of nanoparticles
Laser

\[ \lambda_{\text{ex}} = 800 \text{ nm} \]

\[ \lambda_{\text{ex}} = 267 \text{ nm} \]

Intensity (a. u.)

Wavelength (nm)

Fluorescence

Faraday rotation

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

Spectral Hole-burning

Rare-earth in Glasses

Hole

Laser

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

Faraday rotation

Incident light

Sample

Magnetic field \( B \)

Polarizer

Analyzer

Wavelength of transmitted light
Self-Assembling of Nano-Particles and Nonlinear Optics

Spectral Hole-burning

Shape-Control

Nanoparticles

Self-Assembly

Morphology-Control

\( \chi^{(3)} \) (10\(^{-11}\) esu.)
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
\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]

Cathode
\[ 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]

Total
\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]

High efficiency, Clean energy

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

\[ \text{Si(OC}_2\text{H}_5)_4 \]

\[ \text{H}_2\text{O, EtOH and HCl} \]

Stirring

Drying at R.T.

\[ \text{Gel} \]

Heat Treatment

Porous Glass
Porous structure of the sol-gel-derived glasses

**Porous properties of the glass**

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

Porous network containing SiOH bonds
Water molecules absorbed in the porous glasses

Exposure to humid atmosphere

SiOH bonds

Hydrogen bonded H$_2$O

Physically adsorbed H$_2$O

Heating or exposure

Physically adsorbed H$_2$O molecules are removed by heating at around 100°C.
Effect of the **physically bonded H$_2$O molecules** on the conductivity

\[ \log \sigma = K \log [\text{H}_2\text{O}] \]
Controlling the amount of the **chemically bonded H$_2$O molecules**

Chemically bonded H$_2$O molecules are removed by heating at around 200$^\circ$C.
Effect of the chemically bonded H$_2$O 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 H₂O.
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

Si(O\text{C}_2\text{H}_5)_4

Catalysts → Reacting → Drying → Gels → Heating → Porous Glasses

Pore size

Silica (Si\text(O}C_2\text{H}_5)_4
Pore size distribution and its effect on the conductivity

![Graph showing pore size distribution and conductivity vs. relative humidity for different samples.]

- No. 1
- No. 2
- No. 3
- No. 4

The dV/d(logD) distribution is shown for each sample, indicating the pore size distribution. The conductivity (log conductivity vs. relative humidity) is also plotted for each sample, demonstrating how relative humidity affects conductivity for different pore sizes.
Effect of the pore size on the proton conductivity

DTA curve for No. 2 glass

Solidification of H$_2$O

= -45°C

Quantum dot effect

Effect of the pore size on the proton conductivity

-60 -40 -20 0 20

Exotherm

Temperature (°C)

Solidification of H$_2$O

DSC curve for No. 2 glass

Quantum dot effect

0 2 4 6 8 10

dV/d(logD) (cm$^3$.g$^{-1}$.nm$^{-1}$)

Pore Diameter (nm)

-30 0 30

Temperature (°C)

-1 -2 -3 -4

log $\sigma$ (S/cm)

1000/T (K$^{-1}$)

1 2 3 4 5 6

No. 3

No. 2

25 2 0 5 0

dV/d(logD) (cm$^3$.g$^{-1}$.nm$^{-1}$)

Pore Diameter (nm)

-60 -40 -20 0 20

Exotherm

Temperature (°C)

Solidification of H$_2$O

= -45°C

Quantum dot effect

Effect of the pore size on the proton conductivity

-30 0 30

Temperature (°C)

-1 -2 -3 -4

log $\sigma$ (S/cm)

1000/T (K$^{-1}$)

1 2 3 4 5 6

No. 3

No. 2
Effect of $\text{P}_2\text{O}_5$ on proton conductivity

$\text{Si(OC}_2\text{H}_5)_4$

Hydrolyzing

Reacting

Drying

Gels

Heating

Porous Glasses

$\text{PO(OCH}_3)_3$

$\text{P}^5+\text{ ion}$
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$_2$O.

- High proton conductivity in wide temperature range
  -30°C to 150°C
  (ex. 170 mS/cm at 150°C)
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

Si(OCH₂CH₃)₄ → Hydrolyzing → Reacting → Drying → Gels → Heating → Porous Glasses

- Templates
- Catalysts

Pore orientation

Pore size

Thin Film

Bulk Glass

Substrate

200nm

5cm
Pore-oriented glass films by self-assembling method

Preparation of glass film by self-assembling method using templates

Solution

CTAB; 
(CH₃(CH₂)₁₅N⁺(CH₃)₃Br

C₁₆EO₁₀; 
(C₁₆H₃₃(OCH₂CH₂)₁₀OH

Dipping → Gel → Heating → Porous glass film
Self-assembled pore-oriented glass films

- (a) C₁₆EO₁₀
  - 200: 4.75
  - 210: 4.44
  - 211: 4.18
  - \( a = 9.50 \text{ nm} \)

- (b) CTAB
  - 100: 2.98

Intensity (Arb. units)

2θ (degrees)

Hexagonal

Cubic

Sub. Glass film

200 nm
Conductivities of pore-oriented glass films

\[ \log_{10} \sigma (\text{S/cm}) \]

Relative Humidity (RH %)

(a) \( \text{C}_{16} \text{EO}_{10} \)

(b) CTAB

\[ \text{I} \quad \text{V} \]

\[ \text{I} \quad \text{V} \]
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.
Application of proton conducting glasses

Sensors

Hydrogen, Humidity

\[ \text{EMF} = \frac{RT}{nF} \ln \frac{P_{H_{II}}}{P_{H_I}} \]

\( H_2 = 2H^+ + 2e^- \)

\( 2H^+ + 2e^- = H_2 \)
Responsibility to $H_2$ gas

\[
EMF = \frac{RT}{nF} \ln(P_H)
\]

$H_2 = 2H^+ + 2e^-$
**Gas sensors ~ Preparation of thin films ~**

**Solid electrolyte**

(組成: 5P₂O₅-95SiO₂)

Si(OC₂H₅)₄, 2-PrOH, HClaq

**Spin coating**

Heat treatment (400°C, 4h)

Glass film

**Reference electrode**

MnO₂+4H⁺+2e⁻ ⇌ Mn²⁺+2H₂O

**P/G stat**

Air or Ar

25 °C

Pt

Glass film

Manganese Oxide

ITO glass substrate

Alcohol vapor
Gas sensing

- 25°C
- 1% H₂
- 1% CH₃OH vapor
- 1% C₂H₅OH vapor
- 0.5% NH₃ vapor
- 1% CH₃COCH₃ vapor

1% CH₃OH vapor in air
High proton conducting glasses for the fuel cell electrolyte

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Cathode
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Total
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High efficiency, Clean energy

Inorganic Sol-gel-derived Glass

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

High stability against the thermal and chemical attacks

Proton conducting membrane

Perfluorosulfonate ionomers (Nafion)
High proton conductivity at around room temperature
Degradation in thermal and chemical attacks
Fuel Cell

![Graph showing the relationship between cell voltage (V), current density (mA/cm²), and power density (mW/cm²). The graph indicates a peak power density of 50.7 mW/cm² at a specific current density.]
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 -30°C to 150°C
    - ex. 170 mS/cm at 150°C
- Glass films having high-ordered pore structure
- Possible application as the electrolyte
  - Sensor and Fuel cell
Thank you