

Ordered mesoporous phosphosilicate glass electrolyte film with low area specific resistivity

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Ordered mesoporous phosphosilicate glass electrolyte film exhibiting low area specific resistivity (ASR) compared with those of Nafion has been synthesized using non-ionic surfactant as the structure-directing agent.

Conductors exhibiting high proton conductivities at low temperature have attracted considerable attention because of their potential use as an essential component-electrolyte in fuel cells.¹⁻⁴ As is well known, area-specific resistivity (ASR, or t/σ , where t is the electrolyte thickness and σ is the conductivity) of the electrolyte should be made as small as possible to ensure high power densities.^{4,5} Polymer electrolyte membrane was fabricated relatively easily to produce satisfactory ASR values. So far, the polymer electrolyte fuel cells (PEFC) is generally considered to be the most viable approach for mobile application. However, it still has some problems for practical use. It is susceptible to deformation based on its adsorption and desorption of water, which complicates the water management of the cell. In addition, its thermal and chemical degradation at about 100 °C or higher would limit its use.

We have been studying proton conductivity in porous glasses.⁶⁻⁸ Recently, using a sol-gel method, we prepared P_2O_5 -containing glasses exhibiting conductivities of $10^{-4} \sim 10^{-2}$ S cm^{-1} over a wide temperature range.⁸⁻¹⁰ Our further interest in this field is the fabrication of fast proton-conducting glass film, which can realize portable fuel cell systems. Previously we reported the control of the pore structure in the film to assure high conductivity.¹¹ Here, using non-ionic surfactant as the structure-directing agent, we succeeded in preparing ordered mesoporous phosphosilicate glass film exhibiting low ASR.

Transparent and crack free $5P_2O_5-95SiO_2$ (mol%) glass films with a thickness of ~ 0.5 μm were prepared using tetraethoxysilane and phosphoric acid.[†] Non-ionic surfactant $C_{16}EO_{10}$ ($C_{16}H_{33}(OCH_2CH_2)_{10}OH$) was used as the structure-directing agent. The porous properties were examined from the nitrogen sorption and desorption isotherm. The phosphosilicate film has a pore size distribution smaller than about 2.5 nm calculated by using the BJH method. The pore surface area and pore volume were determined to be 577 $m^2 g^{-1}$ and 0.31 $ml g^{-1}$, respectively.

Fig. 1 shows X-ray diffraction patterns of as-deposited and 400 °C calcined films. In the as-deposited film (Fig. 1A), four well-resolved diffraction peaks are observed at low angles of $2\theta = 1.5-2.5^\circ$, which can be indexed as (111), (200), (210), and (211) reflections of an ordered cubic (Pm3m) mesostructure. The X-ray diffraction pattern of calcined phosphosilicate film (Fig. 1B) shows that the intense (210) and (211) peaks still remain at higher angles, accompanied by an additional weak (420) second-order reflection. These results reveal that the cubic framework, interconnecting the continuous domain structure in three-dimensional space, is preserved after removing the surfactant along with a shrinkage of the unit cell parameter from 9.64 nm to 7.8 nm. This indicates that the cubic mesoporous film is thermally stable. To the best of our knowledge, this is the first synthesis of a highly ordered mesoporous phosphosilicate film with three-dimensional accessible pore structure.

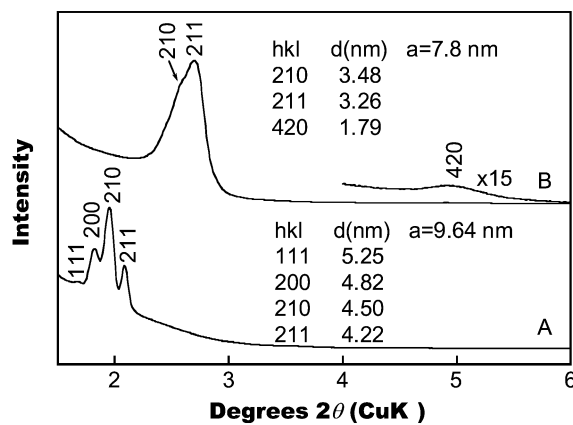


Fig. 1 X-ray diffraction (XRD) patterns of A, as-deposited and B, calcined mesoporous $5P_2O_5-95SiO_2$ film prepared using $C_{16}EO_{10}$ as template, in which H_3PO_4 was used as starting material for P_2O_5 .

Proton-conducting properties of the phosphosilicate glass electrolyte film were determined as a function of both temperature and relative humidity. The ASR values of phosphosilicate electrolyte film are plotted in Fig. 2 as a function of temperature under 70% relative humidity, and compared to those of Nafion membrane.¹² Note that the phosphosilicate film exhibits lower ASR less than $0.4 \Omega cm^2$ between 40 and 80 °C, which are lower than half for Nafion. The activation energy for the proton conduction, determined from the Arrhenius plots of the conductivity data, was about 0.32 eV. The activation energy of proton conducting glasses is related to the energy necessary for the dissociation of a proton from the hydroxy groups in the pore surface.^{6,7}

Fig. 3 shows the relation between the ASR of electrolyte film measured at 50 °C, and the relative humidity. It is evident that the ASR rapidly decreases when the relative humidity increases

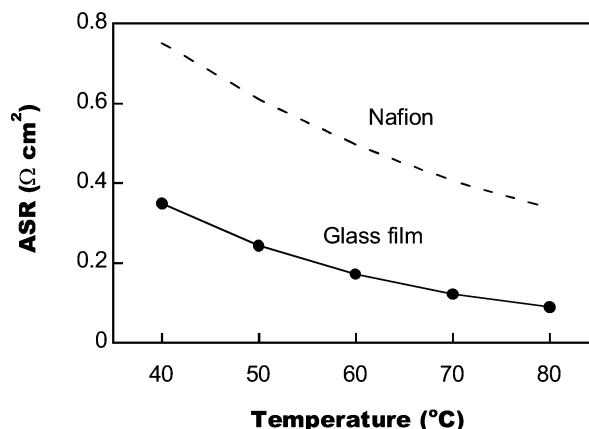


Fig. 2 Changes of ASR as a function of temperature for calcined phosphosilicate films kept in a humid atmosphere at 70% RH. Films thickness is measured as *ca.* 0.5 μm by a surface profilometer. For comparison, we show ASR calculated from a typical membrane thickness of 150 μm for Nafion membrane.¹²

from 40 to 90%. The proton conduction of porous silica glasses is promoted by the dissociation of protons from hydroxy bonds on the pore surfaces and the proton hopping between hydroxy groups and water molecules.^{6,7} Such phosphosilicate mesoporous film with large surface area ($577 \text{ m}^2 \text{ g}^{-1}$) and large pore volume (0.31 ml g^{-1}) possesses the capability of absorbing a large amount of water in the pores. For the phosphosilicate film with cubic pore structures that are connected in a three-dimensional network, water molecules from ambient moisture can enter the film through accessible pore channels and act as the pathway to transfer the protons. As a result, the conductivity of the glass film increases with increasing water content, indicating that the ASR decreases with increasing relative humidity. The ASR values of such phosphosilicate glass electrolyte films are about two orders of magnitude smaller than that of silica film in the literature,¹¹ because the proton in a POH bond is strongly hydrogen bonded with water and is more mobile compared with the SiOH bond.⁸ A very interesting phenomenon in Fig. 3 is that the electrolyte film exhibits low ASR values in the course of decreasing the humidity from 90 to 40% RH, which are maintained even if exposed in low humidity. This result strongly suggests that the film exposed once in high humidity retains the water in the pores and exhibits low ASR values almost irrespective of the humidity change. Note that the film contains pores smaller than 2.5 nm diameter, which is less than that of Nafion membrane with an average diameter of 4 nm.¹³ It is known that when water molecules are confined in a small space, the properties of the water becomes different from that of free water.¹⁴ These confined water molecules are retained in the small pores, so that the ASR values maintain at low level. This is very important for use in the actual fuel cell as electrolyte membrane, because it can simplify the water management, and consequently decrease the cost.

In summary, we successfully prepared proton-conducting phosphosilicate film with ordered pore structure. Such film exhibits low ASR values at low temperature as proton conducting electrolyte. Additional research, such as stability

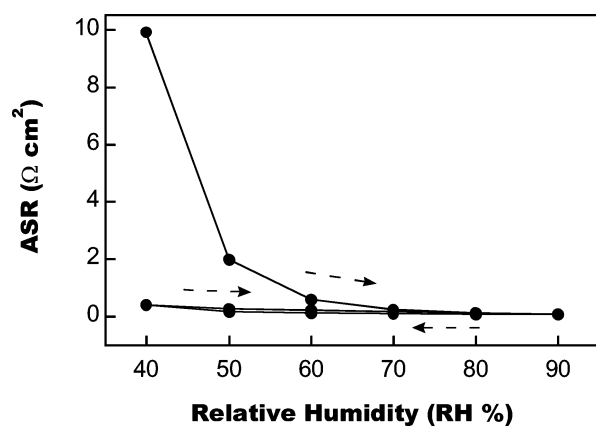


Fig. 3 Changes of ASR as a function of relative humidity for calcined phosphosilicate films with an exposure to water vapor at 50 °C. The arrows indicate the direction of change on relative humidity.

over time and electrode kinetics *etc.* is clearly necessary for practical application in a fuel cell; however, the electrolyte film with steady ASR values under low humidity described here is very encouraging, implying comfortable water management and significant reduction of manufacturing cost as a fuel cell electrolyte.

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Notes and references

† Non-ionic surfactant $\text{C}_{16}\text{EO}_{10}$ ($\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$) was used as the structure-directing agent. First, tetraethoxysilane (TEOS), propanol, water and HCl in the $1:3.8:1:8 \times 10^{-5}$ molar ratios were mixed for 1 h at 60 °C. After adding the additional water and HCl, the sol was further stirred for 1 h at 70 °C. The surfactant solution was separately prepared by dissolving the surfactant in propanol, with stirring at room temperature for 1h. Phosphoric acid was added in the solution, followed by stirring for 1h. And then the resultant solution was slowly added under stirring to the previously prepared sol. The sol was then stirred for another 1 h at room temperature. The final reactant mole ratios were 1 TEOS:11.4 propanol: 5 H_2O :0.004 HCl:0.1 surfactant:0.105 phosphoric acid. An ITO glass sheet was used as the substrate. Prior to deposition, the substrate was degreased with a neutral detergent, washed ultrasonically in distilled water and then rinsed with acetone. The phosphosilicate gel film was deposited by dipping the substrate into the sol and withdrawing at a constant rate of 30 cm min^{-1} , followed by heating at 400 °C for 6 h under nitrogen to remove the surfactants. Transparent and crack free $5\text{P}_2\text{O}_5\text{-}95\text{SiO}_2$ glass films with a thickness of $\sim 0.5 \mu\text{m}$ were obtained. The thickness of the film can be varied from 100 nm to 1 μm by adjusting the dip-coating rate.

The XRD patterns were recorded on a Philips X'Pert-MPD diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation at 50 kV and 40 mA. Au top electrodes with 0.3 cm diameter were sputtered on the surface of film through a shadow mask. The proton conducting properties of the films were determined using an impedance analyzer (Solartron, SI-1260) with an amplitude of 50 mV.

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