

New Composite Membranes for Low-Temperature Fuel Cells

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To obtain high proton-conducting polymer electrolyte membrane (PEM) materials that are simple to fabricate and are cheap, two types of organic-inorganic hybrid composites were fabricated: silicophosphate (SiP) - PMA (molibdo-phosphoric acid), SiP-PWA (tungsto-phosphoric acid), and α -zirconium phosphate (ZrP) - polytetrafluoroethylene (PTFE), and γ -ZrP-PTFE.

SiP-PMA and SiP-PWA gels were synthesized by incorporating PMA or PWA as a proton source in an amorphous silicophosphate gel structure. The obtained gels were homogeneous and chemically stable. For both gels of SiP-PWA and SiP-PMA, proton conductivity increased up to over $1.9 \times 10^{-3} \text{ S/cm}$ as PMA(PWA) concentration increased.

High proton-conductivity was also observed in the polytetrafluoroethylene (PTFE) - based composites with either α - or γ - zirconium phosphate (ZrP) powder dispersed in grain boundaries of PTFE polymer particles. By addition of ZrP, the proton conductivity increased from 10^{-13} S/cm to $2.2 \times 10^{-3} \text{ S/cm}$.

All of the fabricated composites in this study showed high chemical stability in water and high mechanical strength due to oxide- or polymer-network formation.

Key words : proton, PEFC, PEM, composite, PMA, PWA, ZrP

1. INTRODUCTION

As the most practical fuel cell candidate, solid polymer electrolyte fuel cells (PEFCs) are receiving attention due to their low operating temperature, non-production of CO_2 and suitability for electric vehicles.

Electrolyte material in PEFCs needs to have (a) high specific conductivity, (b) good mechanical and chemical stability, and (c) low cost ($< \$200/\text{m}^2$) [1]. A polymer electrolyte membrane (PEM) in PEFC is an electronic insulator, but is also an excellent conductor of hydrogen ions. A PEM is used in the form of $50\mu\text{m}$ - $200\mu\text{m}$ -thick membrane and works as a gas separator and also as an electrolyte. The electrolyte and electrodes are pressed together to produce a single membrane-electrode assembly (MEA). The membranes developed by DuPont (Nafion series) and Dow are most widely used. Both these membranes consist of perfluorinated copolymers with sulfonic-acid functionalized side chains. However, these materials are expensive and have complicated synthetic procedures.

To obtain high proton-conducting PEM materials that are simple to fabricate and are cheap, we investigated fabrication and characterization of new organic-inorganic hybrids. The inorganic-organic hybrids are one of the most promising materials because they possess both inorganic and organic functionality. These materials have been synthesized by utilizing the low temperature reaction of the sol-gel process. Some of these materials fabricated by copolymerization of metal alkoxides and organic-substituted silicon alkoxides or organic-based oligomers have been reported as 'ORMOSILs' and 'CERAMER' [2]. Incorporation of other inorganic species in the hybrid materials is used to control the chemical and physical properties, and also makes it possible to expand their application field. Despite of many advantages of the organic-inorganic hybrid materials, e. g., high functionality, high chemical and thermal stability, and simple processing,

few attempts have been made to develop these materials for proton-conducting electrolytes.

Here, we fabricated two types of fast proton-conducting organic-inorganic hybrid composites:

(a) *Silicophosphate-PWA(PMA) hybrid gels*
(SiP-PWA(PMA)):

Either Tungsto-phosphoric acid (PWA, $\text{H}_3[\text{W}_{12}\text{PO}_{40}] \cdot 29\text{H}_2\text{O}$) or molibdo-phosphoric acid (PMA, $\text{H}_3[\text{Mo}_{12}\text{PO}_{40}] \cdot 29\text{H}_2\text{O}$), which are representative solid acids having high proton conductivity of about $2 \times 10^{-1} \text{ S/cm}$ at 25°C [3], was incorporated as a proton source in silicophosphate amorphous gel structure. To study the effect of acid concentration on proton conductivity, we used low concentration (PWA(PMA)/Si molar ratio = 0.005) and high concentration (PWA(PMA)/Si molar ratio = 0.08)

(b) *α - or γ - zirconium phosphate (ZrP) - polytetrafluoroethylene (PTFE) composites*
(ZrP-PTFE) :

Zirconium phosphate (ZrP) is a well-known two dimensional layer-structured compound. The intercalation property and relatively high proton-conductivity makes this compound more attractive for electrical applications. Reported proton conductivity for α -ZrP($\text{Zr}(\text{HPO}_4) \cdot \text{H}_2\text{O}$) single crystals is about $\sim 10^{-5} \text{ S/cm}$ [6]. However, Ablerti et al. [7] found that the mobility of surface ions in α -ZrP is 10^4 times higher than those of interlayer ions, and that the low activation energy ($11 \sim 13 \text{ kJ/mol}$) for ionic conduction was due to the transport of surface ions. Therefore, the surface ions of layer-structured ZrP compound significantly contribute to the total conduction, although the fraction of the carriers present on the surface is very small. Furthermore, both α -ZrP and γ -ZrP show high

chemical stability in water. The application of the high surface ion mobility of ZrP in the field of PEFC requires that fine ZrP particles be fixed in the electrolyte material to increase the specific surface area in the composite. In our study, we used partially polymerized PTFE particles as a fixing matrix.

To study the effect of electrical anisotropy on proton conductivity, we applied low pressure (0.1MPa) and high pressure (10MPa).

We also characterized bonding structure of hydroxyl groups and water, and microstructure of these composites by using FT-IR(Fourier transform-infrared spectroscopy), XRD(X-ray diffractometry), FE-SEM(Field emission scanning electron microscopy).

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation and Characterization

SiP-PMA(PWA) gels were prepared by using tetraethoxysilane (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$, 1mol), diisopropyl phosphate ($\text{HP}(\text{OC}_3\text{H}_7)_2$, 0.5mol) and ethanol as starting materials. After 30 minutes of stirring, 0.005mol - 0.08mol of PWA or PMA was added to this starting solution. After 1mol of di-methylformamide (DMF) was added as a drying condition control agent, 1.5mol of distilled water diluted with ethanol was added to the mixed solution for hydrolysis reaction. The obtained clear precursor solution was allowed to gelate for 3 days at 23°C and 13%RH.

α -ZrP-PTFE and γ -ZrP-PTFE composites were prepared using the PTFE emulsion (60wt%, grain size: 0.2 μm -0.4 μm), guaranteed-grade commercial α -ZrP ($\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$) and γ -ZrP ($\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$) crystalline powders (Daiichi Kigenso Kagaku Kogyo Co. Ltd), respectively, as starting materials. Fast agglomeration and polymerization of PTFE occurred during mixing the starting materials. Each sample composition was 50wt% of either α -ZrP or γ -ZrP. After drying at 80°C for 3 hrs, each composite was pressed at either 0.1MPa or 10MPa. Bulk composites were obtained after drying at 80°C and heat-treating at 150°C for 1 hr.

The FT-IR absorption spectra were measured with an FT-IR spectrometer (Perkin Elmer model Spectrum BX) connected to a PC, at room temperature using specimens with a thickness of 200 μm . All of the samples

were immersed in water for 1 hr before the measurement. Phase analysis was performed with X-ray diffractometry (Philips) using $\text{CuK}\alpha$ radiation at room temperature. A field emission scanning electron micrograph (Hitachi model S4100) was used to observe the microstructures.

2.2 Proton Conductivity Measurement

The conductivity of each fabricated composite was obtained from Cole-Cole plots by using an ac method involving an impedance analyzer (IM6 impedance measurement system, Zhaner Electric Co.) with platinum plate electrodes fixed on either side of the sample. The conductivity measurements were carried out at 23°C, and all of the samples were immersed in distilled water for 10 minutes and the water on the samples were removed before the measurement.

For ZrP-PTFE composites, conductivity was measured with the electrodes placed perpendicular($\perp$) and parallel($\parallel$) to direction of the applied pressure to study grain orientation effect of ZrP crystalline.

3. RESULTS AND DISCUSSION

3.1 Silicophosphate-PMA(PWA) Gels (SiP-PMA(PWA))

Fig. 1 shows photographs of the obtained SiP-PMA(PWA) gels. The samples prepared with a small amount of PMA(PWA) (PWA(PMA)/Si molar ratio = 0.005) were translucent and rigid, whereas those prepared with a large amount of PMA(PWA) (PWA(PMA)/Si molar ratio = 0.08) were opaque and brittle. All of the samples were stable in water, despite the high solubility of PMA and PWA in water. SiP-PMA was yellowish green, and SiP-PWA was transparent at 0.005mol of PWA and was white at 0.08mol of PWA. All of the samples showed cracks on the surface of the samples during drying, resulting in the sample breakdown into several pieces. Fig. 2 shows FT-IR patterns of SiP-PMA and SiP-PWA gels. Scholze [4] found that there are three main IR absorption bands due to hydroxyl groups, i.e., band-1 in the range of 3640 cm^{-1} -3900 cm^{-1} , band-2 around 2900 cm^{-1} and band-3 at 2340 cm^{-1} . However, the existence of the band-3 is not certain yet and various absorption bands due to network formers are overlapped. Band-1 is due to hydrogen bonding-free hydroxyl groups and band-2 is to strongly hydrogen-bonded hydroxyl groups. It has been reported that protons in band-2 are much more mobile

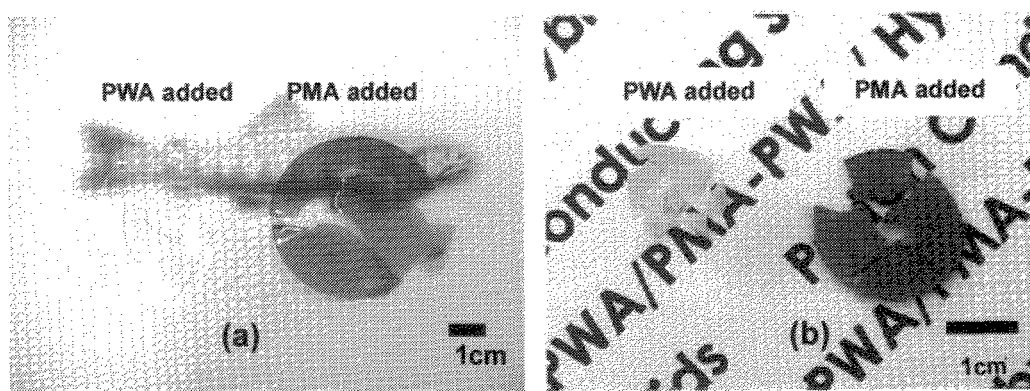


Fig. 1. Photographs of SiP-PMA(PWA) gels at PMA(PWA)/Si molar ratio of (a)0.005 and (b) 0.08.

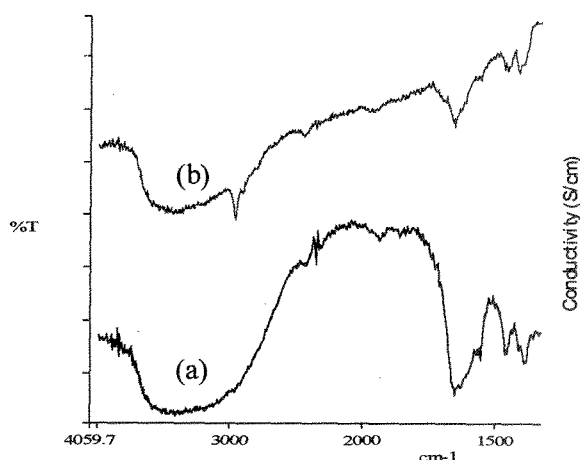


Fig. 2. FT-IR spectra of (a) SiP-PMA (PMA/Si = 0.08) and (b) SiP-PWA (PWA/Si = 0.08).

than those in band-1. These three bands due to hydroxyl group and an absorption peak due to molecular water around 1600cm^{-1} are observed in the IR patterns of both gels.

Fig. 3 shows the measured conductivities of SiP-PMA and SiP-PWA gels. High proton conductivities were measured for the composition of PMA(PWA)/Si=0.08: $1.9 \times 10^{-3}\text{S/cm}$ for SiP-PWA and $5.5 \times 10^{-3}\text{S/cm}$ for SiP-PMA. The conductivity increased 1000-fold when the PMA(PWA)/Si molar ratio increased from 0.005 (Fig. 3a and b) to 0.08 (Fig. 3c and d). This increase means that the SiP-PMA(PWA) hybrid gels contained trapped solid acids (PMA or PWA) as a proton source and hydroxyl groups bonded to P-O-Si bonds that work as a proton conduction path. The molecular water which is contained in gel structure also provides high proton mobility attributing an increase of proton conductivity. According to Abe et al. [5], the activation energies for the dissociation or ionization of protons in hydroxyl groups are essentially the same when the values for ν_{OH} (peak wavenumber of the infrared absorption band due to fundamental O-H stretching vibration) are the same, but the activation energies for transport (proton hopping) are different. That is, the activation energy for hopping through molecular water is much less than that for hopping through non-bridging oxygen. This improved proton mobility due to molecular water may be another advantage of sol-gel derived proton conducting materials.

3.3 α -ZrP-PTFE and γ -ZrP-PTFE composites

Fig. 4 shows the XRD patterns of commercial PTFE film, α -ZrP-PTFE and γ -ZrP-PTFE composites fabricated by pressing dried composite powders at a pressure of 0.1MPa. Both the α -ZrP-PTFE (Fig. 4b) and γ -ZrP-PTFE (Fig. 4c) composites exhibited mixed phases of α -ZrP and PTFE, and γ -ZrP and PTFE, respectively.

The microstructures of γ -ZrP-PTFE composite are shown in Fig. 5. The particle sizes ranged from $0.5\mu\text{m}$ to $1\mu\text{m}$ for α -ZrP, and from $5\mu\text{m}$ to $15\mu\text{m}$ for γ -ZrP. Many thread-like PTFE polymers can be observed in the cross-sections of the sample indicating occurrence of polymerization reaction of PTFE at room temperature in

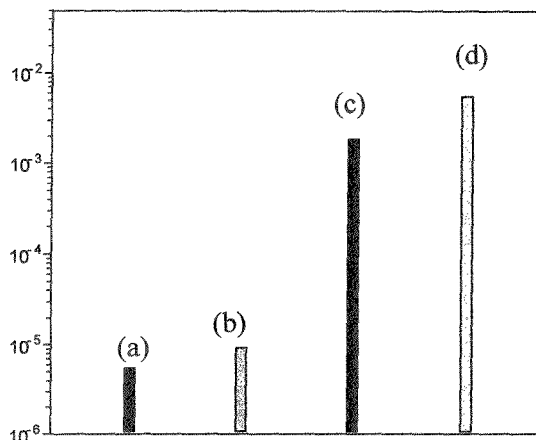


Fig. 3. Conductivity of the obtained samples ; (a) SiP-PWA (PWA/Si = 0.005), (b) SiP-PMA (PMA/Si = 0.005), (c) SiP-PWA (PWA/Si = 0.08), (d) SiP-PMA (PMA/Si = 0.08).

the ZrP-PTFE composites. Due to these polymer networks, a sufficient mechanical strength for electrical measurement and flexibility were achieved.

Fig. 6 shows the measured conductivities of the ZrP-PTFE composites. By addition of ZrP, the proton conductivity of PTFE increased from 10^{-13}S/cm (Fig. 6a) to above 10^{-4}S/cm which is higher than that for ZrP single crystals (about 10^{-5}S/cm). Such high proton conductivity might be due to the high ion mobility on the surface of ZrP particles. Our results also show that the proton conductivity of ZrP-PTFE composites was dependent on the orientation of the electrodes. This orientation-dependant change in the proton conductivity is due to the anisotropy of the two-dimensional ZrP crystal structure. However, the proton conductivity of γ -ZrP-PTFE composite prepared at 0.1MPa with parallel electrodes ($2.2 \times 10^{-3}\text{S/cm}$, Fig. 6f) was higher than that prepared at 10MPa with perpendicular electrodes ($1.2 \times 10^{-3}\text{S/cm}$, Fig. 6e). This higher conductivity might be due to low density of the sample causing an increase of water absorption.

4. SUMMARY

Two types of high proton-conducting inorganic-organic hybrids in silicophosphate-PMA(PWA) (SiP-PMA(PWA)) hybrid gels and in α -(γ -) ZrP-PTFE were successfully fabricated. All of the samples showed mechanical strength sufficient for measuring the proton conductivity.

Obtained SiP-PMA/PWA hybrid gels were brittle and had cracks. However, the proton conductivities of these materials were high, and increased about 1000-fold with increasing PMA(PWA)/Si molar ratio from 0.005 to 0.08. At PMA(PWA)/Si = 0.08, the measured conductivity was $1.9 \times 10^{-3}\text{S/cm}$ for SiP-PWA and $5.5 \times 10^{-3}\text{S/cm}$ for SiP-PMA, respectively. Such high proton conductivity might be due to the nanostructure, which contained both the trapped solid acids (PMA or PWA) as a proton source and contained the hydroxyl groups bonded to P-O-Si oxide bonds that work as a proton conduction path. Moreover, the molecular water contained in a gel structure also provided high proton mobility, resulting in an increase in proton conductivity.

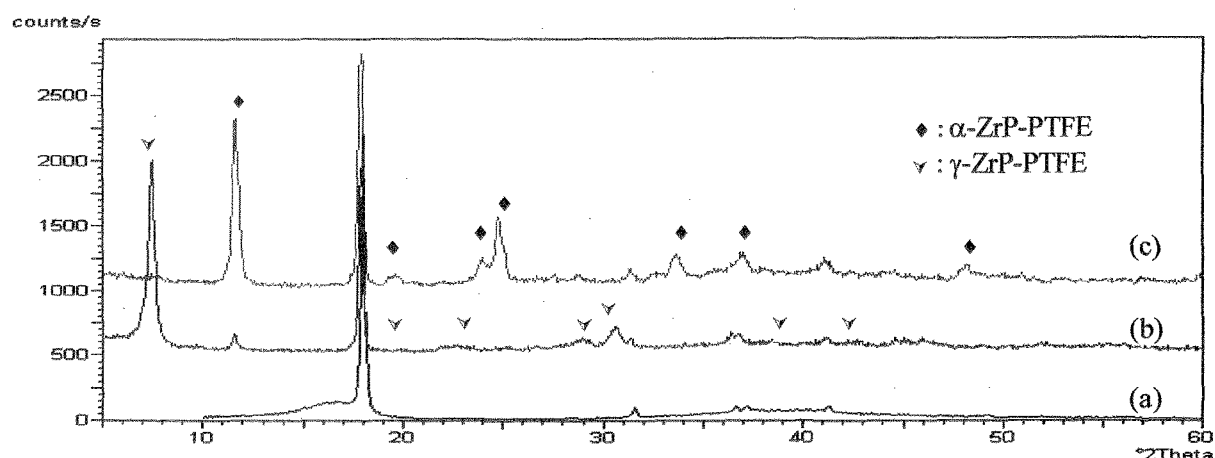


Fig. 4. XRD patterns of (a) commercial PTFE film, (b) α -ZrP-PTFE composite and (c) γ -ZrP-PTFE composite.

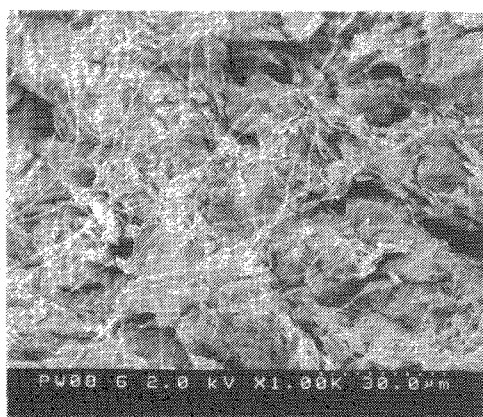


Fig. 5. SEM images of γ -ZrP-PTFE composites.

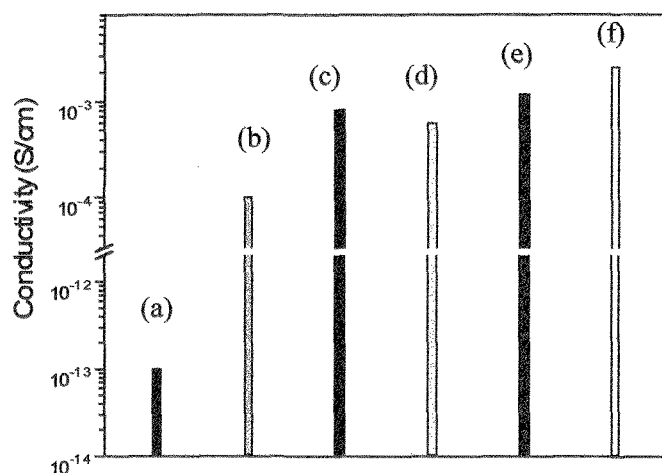


Fig. 6. Conductivity of the obtained ZrP-PTFE composites; (a) commercial PTFE film, (b) α -ZrP-PTFE ($\parallel$, 10MPa), (c) α -ZrP-PTFE ($\perp$, 10MPa), (d) γ -ZrP-PTFE ($\parallel$, 10MPa), (e) γ -ZrP-PTFE ($\perp$, 10MPa), (f) γ -ZrP-PTFE ($\parallel$, 0.1MPa). ($\perp$ and $\parallel$ represent electrodes placed perpendicular ($\perp$) and parallel ($\parallel$) to direction of the applied pressure, respectively.)

In the ZrP-PTFE composites, the measured conductivities of α -ZrP-PTFE and γ -ZrP-PTFE composites increased from 10^{-13} S/cm of PTFE to over 10^{-3} S/cm. Proton conductivity higher than that for a ZrP single crystal might be due to the high ion mobility associated with the large surface area of the ZrP particles.

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