

## Proton Conducting Behavior of a Novel Composite Based on Phosphosilicate/Poly(Vinyl Alcohol)

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### ABSTRACT

A series of proton conductive composite membranes based on poly(vinyl alcohol) and phosphosilicate gels powders were successfully prepared. The proton conductivity of these composite was attributed to the phosphosilicate gel, which derived from tetraethoxysilane and phosphoric acid by sol-gel process at a molar ratio of P/Si = 1.5. The proton conductivity increased with increasing both the content of phosphosilicate gel and relative humidity. Temperature dependence of conductivity showed a Vogel-Tamman-Fulcher type behavior, indicating that proton was transferred through a liquidlike phase formed in micropores of phosphosilicate gel. The high conductivity of 0.065 S/cm with a membrane containing 60 wt% of the gel was obtained at 60°C at 90% relative humidity.

**Key words :** Proton conductivity, Solid state electrolyte, Sol-gel, Phosphosilicate gel, Fuel cell

### 1. Introduction

The solid state electrolytes have been intensively investigated for their wide application for electrochemical devices, such as fuel cell, gas sensor and capacitor.<sup>1-3)</sup> From a point of practical application, the solid electrolytes should be not only highly conductive, but also a good separator for the fuel and oxidant. However, large-scale applications of per-fluorinated ionomer membrane, such as Nafion<sup>®</sup> membranes are limited by the high cost and poor barrier to methanol crossover. So it is very necessary to search for novel proton conductive membranes with low cost and low methanol permeability.

Recently, the phosphosilicate gels prepared by sol-gel process have been found to exhibit high conductivity.<sup>4-6)</sup> These gel materials containing a large number of micropores and mesopores filled with "liquid" for fast proton transportation. Moreover, the gel materials show higher thermal stability and lower humidity dependence than that of heteropolyacid.<sup>6)</sup> However, the molding properties of these gel materials should be improved for practical applications to electrochemical devices. In view of the above, the phosphosilicate/poly (vinyl alcohol) (PVA) composite membranes with high conductivity, good molding property, and low methanol permeability have been prepared in this work. These nanocomposite materials with an inorganic glass and an organic polymer constitute a relatively new and unique area in material science, which sometimes referred to as "creamers," "organoceramics" or "ormocers".<sup>7)</sup> PVA has been widely used as membrane materials due to the good film-

forming property, high chemical resistance, and high hydrophilicity,<sup>8-10)</sup> especially due to a good barrier for methanol crossover.<sup>11)</sup> Pivovar *et al.*<sup>12)</sup> studied the methanol permeability and proton conductivity of pervaporation membranes. Nafion<sup>®</sup> is an excellent proton conductor but a poor methanol barrier. PVA membranes are good methanol barriers but not appropriate at high temperature. In this paper, the thermal stability is expected to be enhanced by the addition of the phosphosilicate gel and we report the membrane preparation and characterization of the conducting behavior of these composites.

### 2. Experiment Procedure

The phosphosilicate gels were prepared by sol-gel process at room temperature using Si(OC<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> (98%, Acros) and H<sub>3</sub>PO<sub>4</sub> (85.0% aqueous solution, reagent grade). Si(OC<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> was diluted in ethanol and hydrolyzed by HCl solution (pH=0.26). After stirring for 10 min, an appropriate amount of H<sub>3</sub>PO<sub>4</sub> was added drop by drop under stirring. The molar ratio of TEOS/ethanol/H<sub>2</sub>O/HCl/H<sub>3</sub>PO<sub>4</sub> = 1/4/4/0.04/1.5. After stirring for another 2 h, the homogeneous sol was dried at 60°C until gelation and further dried at 60°C for 1 week. Then phosphosilicate gels were pulverized into powder and then heat-treated at 150°C for 5 h, and then kept in desiccator. PVA(85hydrolyzed with a molecular weight of 88,000 g/mol, Hayashi) was dissolved in deionized water at 90°C and diluted to be 10 wt%. Prior to mixing with PVA solution, phosphosilicate gel powder was further ground into a size less than 50 μm. And then the phosphosilicate gel power was mixed with PVA. Each sample was named according to the phosphosilicate gel power contents such as PSA10, PSA20, PSA40, PSA60, and PS (free PVA). respectively. After stirring at room temperature for 12 h, the homoge-

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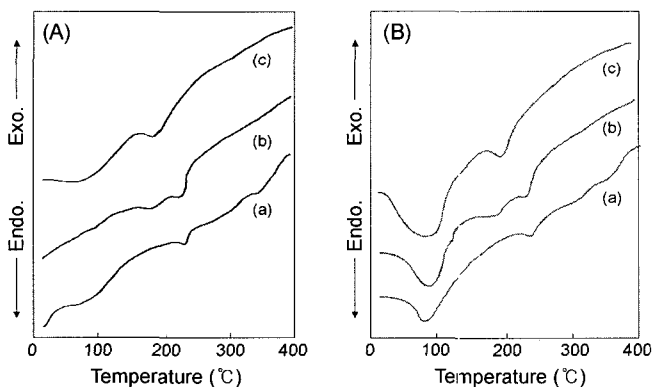
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neous mixture was cast onto Teflon petri dish then dried at room temperature to form a membrane with a thickness about 0.2–0.5 mm, and further dried at 60°C for 24 h, finally kept in dry conditions.

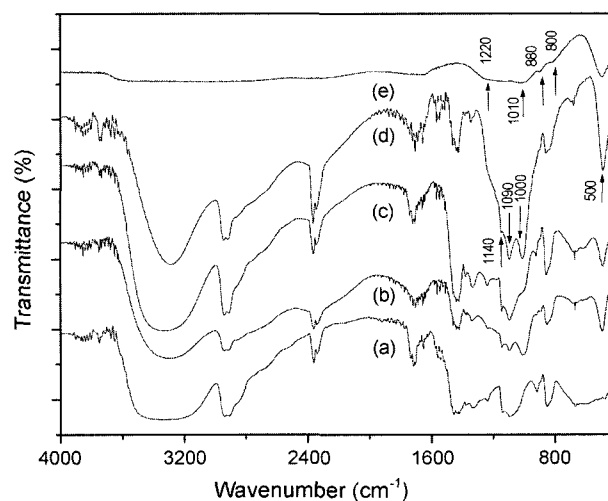
Thermal stability was determined by TG-DTA at a heating rate of 10°C/min in air (TG 8110, Rigaku). Fourier Transform Infrared (FT-IR) spectra were obtained on an infrared spectrophotometer (FTS-3000MX, Bio-rad). X-Ray Diffraction (XRD) patterns of samples were obtained with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation (XD-D1, Shimadzu). The ac conductivity was determined from Cole-Cole plot obtained with an impedance analyzer (HP4192A, Hewlett Packard) in a frequency range of 10 Hz–10 MHz. Silver coated membranes with a thickness about 0.2 mm were sandwiched between the two similar brass electrodes of a spring-loading sample holder. All the impedance data were recorded after the resistance became constant for at least 2 h in a temperature-and humidity-controlled chamber.

### 3. Results and Discussion

The flexible and self-standing membranes with a thickness of 0.10–0.50 mm were easily prepared by solution casting. When the content of phosphosilicate gel is higher than 60 wt%, the composite is brittle and readily crack. Fig. 1 shows the DTA curves for membranes before (Fig. 1(A)) and after (Fig. 1(B)) a treatment at 25°C under 60%R.H for 24 h. As can be seen from the figure, these composite membranes are thermally stable in the temperature range below 400°C without decomposition. The endothermic peak centered at about 100°C is attributed to evaporation of water physically absorbed in the membranes, which became more pronounced after storage in 60%R.H condition for 24 h. And water content increased with increasing the content of phosphosilicate gel in the membrane. This result suggests that the composite can absorb water molecule from the ambient into micropores in phosphosilicate gels. The endothermic peaks at about 190°C and 230°C are due to the dehydration of H $_3$ PO $_4$  and hydroxyl groups of PVA chain, respectively.



**Fig. 1.** DTA curves for the membranes : (a) PVA, (b) PSA20, and (c) PSA60 before (A) and after (B) a treatment at 25°C under 60%R.H for 24 h.



**Fig. 2.** Infrared spectra of pure PVA (a), PVA/H $_3$ PO $_4$  (8/2 in weight) (b), PSA20 (c), PSA60 (d), and PS (e).

When the content of phosphosilicate gel increased to 60 wt%, the endothermic peaks of H $_3$ PO $_4$  is shifted to about 210°C, at the same time, the dehydration of hydroxyl group is not obvious, indicating the improvement of thermal stability of composite membrane due to the presence of inorganic fillers.

Fig. 2 shows the FT-IR spectra of membranes with different compositions. For comparison, H $_3$ PO $_4$ -doped PVA membrane is also shown in Fig. 2(b). The phosphosilicate gel shows a characteristic band of at 800 and 880 cm $^{-1}$ , assigning to the  $\nu_s$  (Si-O-Si(H)). And a broad absorption band from 1080 to 1220 cm $^{-1}$  is assigned to the  $\nu_{as}$  (Si-O-Si). There is a new band at 1010 cm $^{-1}$  is observed, which is due to the  $\nu$  (P-O-Si). For the composite membrane, an absorption band at 1000 cm $^{-1}$  and 1140 cm $^{-1}$  are observed, assigning to  $\nu$  (PO) in H $_3$ PO $_4$  and  $\nu$  (P=O) in H $_3$ PO $_4$ , respectively.<sup>13)</sup> And the absorption band at 500 cm $^{-1}$  and 1090 cm $^{-1}$ , assigning to (PO $_2$ ) in H $_2$ PO $_4^-$  and  $\nu_s$  (PO $_2$ ) in H $_3$ PO $_4^-$ , respectively. These results suggest the presence of the free H $_3$ PO $_4$  and its dissociation due to the interstitial water phase. According to Matsuda *et al.*<sup>6)</sup> most of the H $_3$ PO $_4$  in the phosphosilicate gel is in isolated form after a storage in humid condition, so we supposed that H $_3$ PO $_4$  was distributed both in PVA phase and micropores of phosphosilicate gel. The former one is due to the H $_3$ PO $_4$  leaching from gel material into PVA solution during mixing process and increased proportionally to the content of gel content in the composite. This is confirmed by increase in intensity of absorption at 1000 cm $^{-1}$  with 60 wt% gel content in comparison to that with a 20 wt% gel content. The latter just shows a shoulder peak at 1000 cm $^{-1}$ . These two kinds of H $_3$ PO $_4$  distributed in composite membrane are expected to contribute to proton conductivity by different mechanisms.<sup>14,15)</sup>

Fig. 3 shows the XRD patterns of composite membranes in the range from 5 to 60°. As can be seen that the phosphosilicate gel heat-treated at 150°C for 5 h is almost amorphous, showing a broad amorphous halo entered at about 21°. The

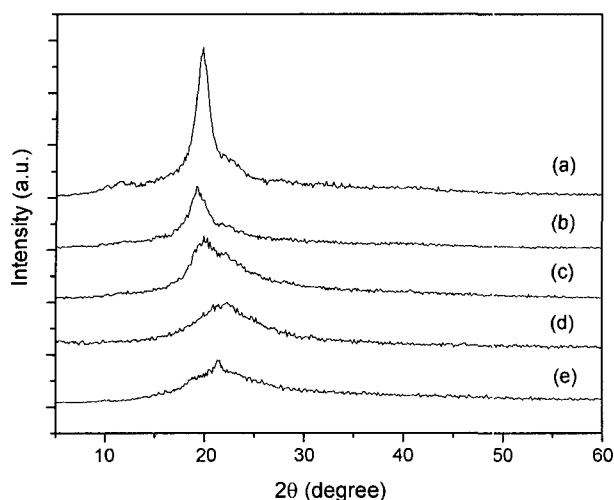


Fig. 3. XRD patterns for membranes : (a) PVA, (b) PSA20, (c) PSA40, (d) PSA60, and (e) PS.

small diffraction peak at  $21^\circ$  may attributed to a small quantity of crystalline  $\text{Si}_5\text{O}(\text{PO}_4)_6$ , which readily hydrolyzed to form isolated phosphoric acid.<sup>6)</sup> However, PVA membrane shows a characteristic for an orthorhombic lattice centered at  $20^\circ$ , indicating a semicrystalline structure of the membrane.<sup>16)</sup> With the content of the phosphosilicate gel increasing, the degree of crystallinity decreases. When the phosphosilicate content is 60 wt%, there is no obvious crystalline structure of PVA in the membrane. This result indicates that crystalline behavior of PVA has been blocked by the inorganic filler, and shows a homogeneous distribution in the composite.

Fig. 4 shows temperature dependence of conduction of composite membrane at 5% R.H in the temperature range from 20 to  $110^\circ\text{C}$ . Temperature dependence of the conduc-

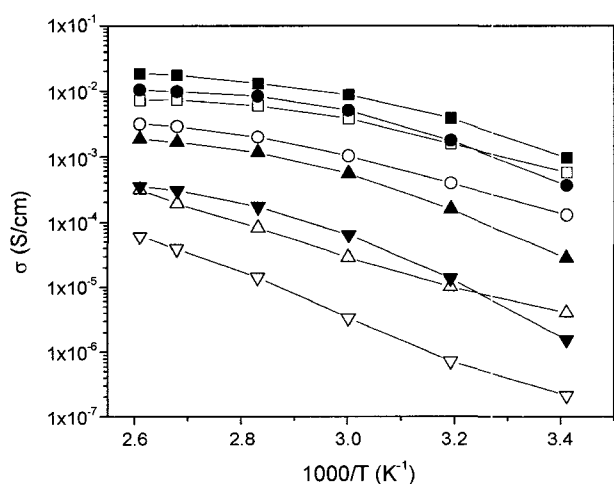


Fig. 4. Temperature dependence of conductivity with different phosphosilicate content at 5%R.H. Close symbols and open symbols represent the membrane before and after storage at  $25^\circ\text{C}$ , 60% R.H for 24 h prior to conductivity measurement respectively.

■/□: PSA60; ●/○: PSA40; ▲/△: PSA20; ▼/▽: PSA10.

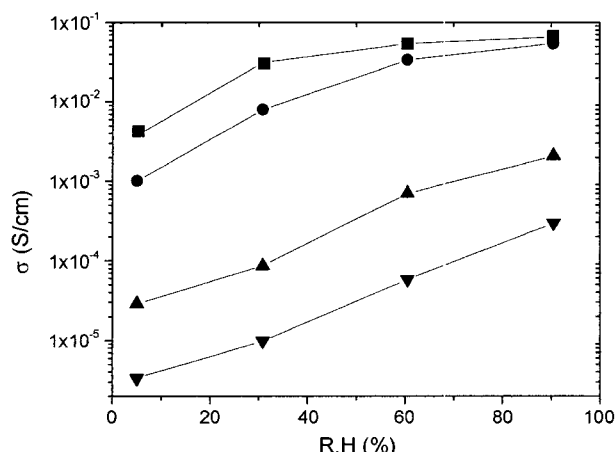
tivity in solid polymer electrolyte has often been taken as indicative of a particular type of conduction mechanism. The dependence of proton conductivity on temperature follows two different types of equations according to two different kinds of proton transport mechanism.<sup>1,12)</sup> One is the hopping mechanism, wherein a proton is transferred through a chain of water molecules by hydrogen bondings, which can be described by Arrhenius equation (Eq. (1)); the other one is the vehicle mechanism, wherein a proton combines with solvent molecules, transferring like liquid phase electrolyte, which followed Vogel-Tamman-Fulcher (VTF) equation (Eq. (2)). The equations are shown as follows:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

$$\sigma = A \exp\left(-\frac{B}{R(T-T_0)}\right) \quad (2)$$

Where  $\sigma_0$  is the pre-exponential factor,  $E_a$  the apparent activation energy,  $R$  the gas constant and  $T$  the absolute temperature.  $A$ ,  $B$ , and  $T_0$  are three parameters. These two principal mechanisms essentially reflect the different in nature of the hydrogen bond formed between the protonated species and their environment. As we mentioned above, in these composite membrane,  $\text{H}_3\text{PO}_4$  is distributed both in the PVA phase and micropores of gel material, which will contribute to proton conductivity in different mechanisms.

As can be seen in Fig. 4, before a treatment at  $25^\circ\text{C}$  under 60%R.H for 24 h, the temperature dependence shows roughly Arrhenius type, especially for membrane with a content of phosphosilicate gel lower than 20 wt%, indicating a hopping behavior in the membrane. However, with a water content increase after a treatment, the conducting behavior shows a characteristic of VTF type. For the dry membrane,  $\text{H}_3\text{PO}_4$  in PVA phase, which have an interaction with hydroxyl groups of PVA or with chemically absorbed water, shows an important role on proton conductivity. These protons are transferred mainly by hopping from hydroxyl group or water molecule with the aid of hydrogen bondings.<sup>14)</sup> This behavior is more pronounced when the gel content is lower, because much more  $\text{H}_3\text{PO}_4$  has leached when contacting with larger amount of PVA water solution. After absorption of water from the ambient, especially due to the hydrophilic character of phosphosilicate gel, the liquid-phase was formed in the phosphosilicate structure, which surrounded by interconnected liquid domains. The VTF type suggests that protons are transferred through a liquidlike phase formed in the micropores of the  $\text{H}_3\text{PO}_4$ -doped silica gels.<sup>15)</sup> From these results, we suppose that the proton conductivity is attributed to both transport mechanisms in the membrane. That is, proton transfer between two phosphosilicate gels may more dependent on the strong hydrogen bonding of PVA chain; while in phosphosilicate gels, the proton conductivity occurs by transport of large complexes such as  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$  like electrolyte in liquid-phase formed in the micropores.



**Fig. 5.** Change of proton conductivity under different relative humidity at 60°C. ■ : PSA60; ● : PSA40; ▲ : PSA20; ▼ : PSA10.

Fig. 5 shows the humidity dependence of conductivity at 60°C with different phosphosilicate content in the membranes. As can be seen in Fig. 5, the conductivity increases monotonically with humidity of measurement conditions increasing from 5% to 90% R.H. For membrane with 60 wt% phosphosilicate gel, conductivity increase from  $3.77 \times 10^{-3}$  to  $6.51 \times 10^{-2}$  S/cm with humidity increase from 5% to 90% R.H. With higher content of phosphosilicate gel, humidity shows significant effect on conductivity at lower humidity due to the high content of the micropores, in which the water absorption-desorption equilibrium significantly affected by humidity. When the humidity was increased higher than 60%, the conductivity levels off, indicating filled pores with water molecules have no further effect on the proton transportation. This result suggests a more pronounced effect on proton conductivity with higher porous structure due to the change in water content, which is the important medium for proton transport.

#### 4. Conclusions

A series of proton conductive composite membranes based on PVA and phosphosilicate gel powders have been prepared in this work. With the addition of PVA solution, the composite is easy to be made into a thin film membrane with homogeneous texture and good thermal stability. High proton conductivity of these composite is attributed to the phosphosilicate gel, which are microporous and hygroscopic with large amount of phosphoric acid, resulting in a dependence on the content of gel material and humidity of ambient condition. After a treatment at 25°C under 60%R.H for 24 h, the temperature dependence of conductivity shows a Vogel-Tamman-Fulcher type behavior, indicating that proton is transferred through a liquidlike phase formed in micropores of phosphosilicate gel. The high conductivity of 0.065 S/cm with a membrane containing 60 wt% of the gel was obtained at 60°C at 90% R.H, indicating a good candidate for medium temperature fuel cell.

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