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Proton conducting behavior of a novel polymeric gel membrane based on poly(ethylene oxide)-grafted-poly(methacrylate)

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Abstract

A novel proton conducting polymeric gel membrane that consists of poly(ethylene oxide)-grafted-poly(methacrylate) (PEO-PMA) with poly(ethylene glycol) dimethyl ether (PEGDE) as a plasticizer doped with aqueous phosphoric acid (H_3PO_4) has been prepared and its physicochemical properties were studied in detail. The ionic conductivity was dependent much on the concentration of H_3PO_4, the immersion time, and content of the plasticizer. This type of proton conducting polymeric gels shares not only good mechanical properties but also thermal stability. Maximum conductivities up to 2.6×10^{-2} S cm^{-1} at room temperature (25 °C) and 2.8×10^{-2} S cm^{-1} at 70 °C were obtained for the composition of the polymer matrix to the plasticizer as 35/65 (in mass) after the H_3PO_4 doping from the aqueous solution with 2.93 mol l^{-1}. FT-IR spectra showed that these high proton conductivities are attributed to the presence of excesses free H_3PO_4 in the polymeric gel in addition to the hydrogen-bonded H_3PO_4 to the polymer matrix.

Keywords: Polymeric gel; Proton conduction; Plasticizer; H_3PO_4; FT-IR

1. Introduction

Solid polymer electrolyte fuel cells (SPEFCs) based on proton conducting polymers have been identified as promising power sources for electric vehicles due to its high conductivity and non-polluting characteristics [1–3]. They overcome many drawbacks, such as leakage and difficulty in electrolyte management, that fuel cells with conventional liquid electrolytes possess. In SPEFCs, ion exchange membranes play a vital role on obtaining not only the high ionic conductivity but also thermal and mechanical stabilities. Nafion®, as a typical candidate, is known to be the most successfully used ionic conductor owing to its high proton conductivity (10^{-2} S cm^{-1} or higher) and chemical stability, but its excessive cost (US$ 750 m^{-2}) and unstable properties at high temperature still hinder the complete application of this technology [4]. Whereas proton conducting polymer composites consisting of neutral polymers doped with inorganic acids [5] have high conductivities even below the glass transition temperature, T_g [6]. This type of polymer electrolytes, contrary to Nafion®-type ones, possesses a lot of merits such as low cost (US$ 100 m^{-2}) and high conductivity both in hydrated and dehydrated states (up to 0.1 S cm^{-1}). These low cost materials have many potential applications in a variety of electrochemical devices including fuel cells, electrode coatings, actuators, artificial muscles, and sensors [7]. Hence, the development of cheaper and better proton conducting polymer electrolyte membranes than those of conventional materials is urgently needed.

In this study, we developed a novel proton conducting polymeric gel membrane that consists of poly(ethylene oxide)-grafted-poly(methacrylate) (PEO-PMA) matrix with poly(ethylene glycol) dimethyl ether (PEGDE) as a plasticizer doped with aqueous H_3PO_4 solution. We have previously reported that this type of plasticized polymer system containing rare earth salts exhibited high ionic conductivity of 10^{-4} to 10^{-5} S cm^{-1} at room temperature [8,9]. Due to the hydrophilic characteristics of poly(ethylene oxide) (PEO), it is also possible for PEO-PMA to cast a good proton conductor from strong acid solutions. Experiments show that the proton conducting polymeric gel membrane developed in the present study shares a number of attractive properties, such as a wider optical transparency range, ease of preparation, good mechanical properties, thermal stability, and high proton conductivity at room temperature. Therefore, it is believed that this type of proton-conducting polymeric gel membranes could have a number of electrochemical applications.

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2. Experimental

2.1. Preparation of the polymeric gel electrolyte, PEO-PMA/PEGDE/H_3PO_4

Poly(ethylene oxide) monomethacrylate (PEM) and poly(ethylene oxide) di-methacrylate (PED) (Shin-Nakamura Chemical Co. Ltd.) were used as prepolymers (macromers) for the matrix formation [9]. Poly(ethylene glycol) dimethylether (PEGDE, M_W = ca. 400) (Toho Chemical Co. Ltd.) was added into the mixed solution of the macromers (PEM:PED = 3:1 by molar ratio). This was followed by the addition of 2,2-dimethoxy-2-phenylacetophenone (99% purity) as an initiator and mixing the entire solution to homogeneity. The resulting mixture onto an aluminum plate was then exposed to UV light for polymerization at room temperature to yield cross-linked polymer matrix, PEO-PMA (Fig. 1). The entire operations were carried out under a dry Ar atmosphere. Then the prepared polymeric gel membranes were swollen in H_3PO_4 aqueous solutions with various concentrations and immersion times. In this stage, H_3PO_4 was doped in the polymeric membrane (PEO-PMA/PEGDE/H_3PO_4). The surface moisture on the films was removed carefully by wiping before measurements. Finally, the films were dried at 50 °C under a vacuum up to constant weight, and then the absorption level of H_3PO_4 was determined by measuring the change in mass before and after the immersion. In this paper, H_3PO_4 uptake will be reported as the mass ratio of H_3PO_4 to the net polymer mass. To discuss conveniently, however, we will use the molar concentration of aqueous H_3PO_4 solutions as a parameter influencing the polymer properties.

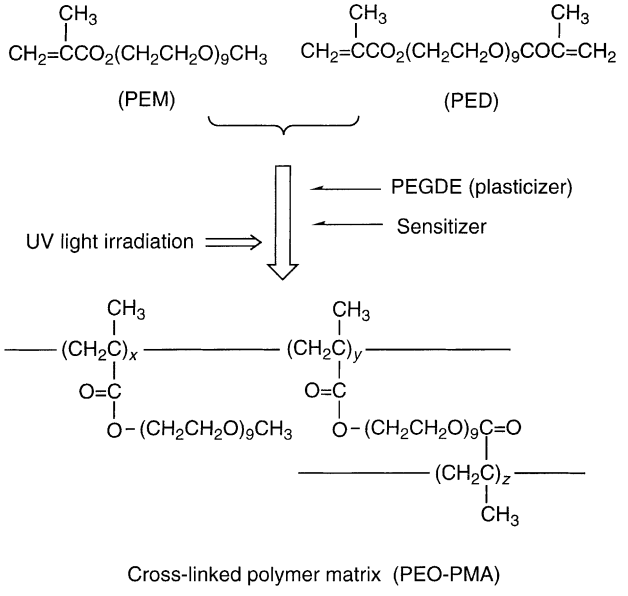


Fig. 1. A scheme for preparation of cross-linked polymer matrix with a plasticizer (PEGDE).

2.2. Conductivity measurements

PEO-PMA/PEGDE/H_3PO_4 complexes were pressed into round disks (13 mm ∅, 60–110 μm thick) at first, then sandwiched between two platinum electrodes packed in a sealed stainless steel cell for conductivity measurements. The ionic conductivity was determined by a complex impedance method done in a frequency range from 100 kHz to 10 Hz using an NF Electronics S-5720C impendence analyzer controlled by a personal computer. Temperature dependence of the conductivity was measured using a model SB-9 EYELA bath under controlled temperature range of 20–70 °C. The atmospheric humidity in the cell will be equilibrated with the water in the gel membrane during the measurements.

2.3. Characterization of PEO-PMA/PEGDE/H_3PO_4 complexes

PEO-PMA/PEGDE/H_3PO_4 complexes were identified by FT-IR spectroscopy (Model FT-IR-4200 spectrometer, Shimadzu Co. Ltd.). The gel films were ground into powder, and the KBr mixtures were pressed into a round disc. FT-IR spectra were recorded with a wavenumber resolution of 2 cm^{-1} in the wavenumber range from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. FT-IR spectrum characteristics of PEO-PMA/PEGDE/H_3PO_4 complexes

The polymeric film (PEO-PMA/PEGDE) was obtained in a self-standing form with sufficient flexibility even after the immersion in aqueous H_3PO_4 solutions [8,9]. An important characteristic of any electrolyte in relation to the ionic conductivity is, in fact, the number of charge carriers. In order to make clear any interactions between the dopant H_3PO_4 and the PEO-PMA matrix, FT-IR spectra were registered in the wavenumber region between 3500 and 400 cm^{-1}, which covers the whole range of all of the IR vibration characteristics. Fig. 2 presents the FT-IR spectra of polymeric gels with and without H_3PO_4 doping that were prepared by immersing the polymeric films with different concentrations of H_3PO_4 aqueous solutions. The absorption peaks at 2900, 1725 and 1115 cm^{-1} are ascribed to the stretching vibrations of C–H, C=O, and C–O bonds in the polymer matrix, respectively [10]. When the polymeric gel films were immersed in aqueous solution of 0.43 mol l^{-1} H_3PO_4, the absorption peak at 1040 cm^{-1} split into two peaks at 1025 and 1002 cm^{-1}. The latter peak comes from the stretching vibration characteristics of P–O(H) bond [10,11]. The intensity of vibration characteristics of P–O(H) bonds increased greatly with an increase in H_3PO_4 concentration. Then the absorption band at 1115 cm^{-1} that comes from the ester group of the polymer matrix was

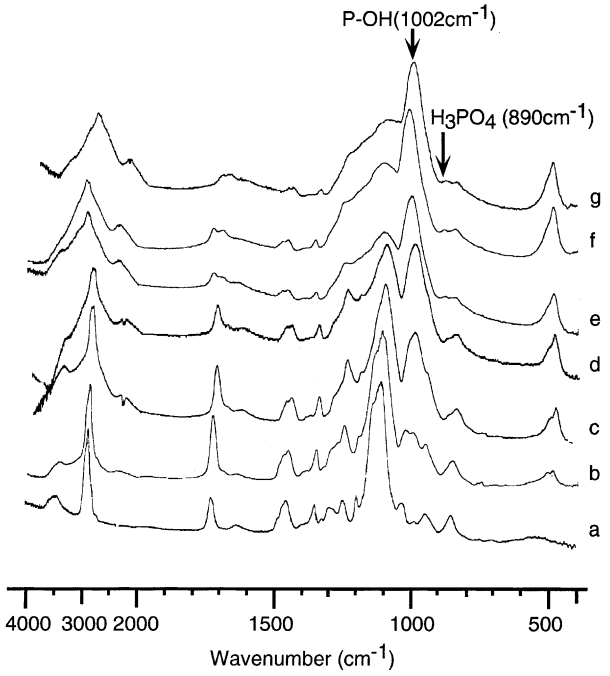


Fig. 2. FT-IR spectra registered for PEO-PMA/H_3PO_4-based gels. The concentration of H_3PO_4 from bottom to top (mol l^{-1}): (a) 0.00; (b) 0.43; (c) 0.85; (d) 1.70; (e) 2.93; (f) 3.57 and (g) 4.69, respectively.

masked by stronger mode due to excess H_3PO_4 when its concentration in the solution was up to 5.95 mol l^{-1}. The absorption peak at 1725 cm^{-1} due to ν(C=O) was weakened and a broad peak centered at 2500–3500 cm^{-1} appeared with increasing the H_3PO_4 concentration. This suggests that the hydrogen bond interaction occurs between O atoms of C=O in the polymer matrix and phosphoric acids. In addition, a new absorption peak at 493 cm^{-1} and a shoulder peak at 890 cm^{-1} appeared and became evident as H_3PO_4 concentration was over 0.85 mol l^{-1}. This result, as well as the fact that the maximal position of the P–O(H) vibrational band of H_3PO_4 was kept at 1002 cm^{-1} over the whole concentration range of H_3PO_4, indicates that the excess free H_3PO_4 is present in the polymeric gels with very weak interaction to the host polymer [10–12].

3.2. Dependence of ionic conductivity on the composition

Fig. 3 shows the ionic conductivity of the PEO-PMA/PEGDE/H_3PO_4 complexes prepared from various H_3PO_4 concentrations as a function of the immersion time. It can be seen that the specific conductivity of the PEO-PMA/PEGDE/H_3PO_4 complex at room temperature depended on the immersion time. It first increased to a maximum at 2–3 h as the samples were soaked in aqueous H_3PO_4 solutions, then decreased with longer immersion time. Similar trends were obtained for the concentration dependence, where the specific conductivity of the samples first increased to a maximum of 2.1×10^{-2} S cm^{-1} as H_3PO_4 concentration was increased from 0.43 to 2.93 mol l^{-1}, then decreased with H_3PO_4 concentration (see Fig. 4). Here, the most of the ionic conductivity would be based on the proton conduction, judging from its magnitude and dependence on the acid concentration in the immersing solution. Due to the hydrophilic characteristics, the polymer could be swollen well in water. Hence, it allows the excess of H_3PO_4 to remain fixed in the interspaces of the gel framework together with water, resulting in the higher proton conductivity. The decreasing trend of the conductivity with longer immersion time (Fig. 3) or higher H_3PO_4 concentration (Fig. 4) is a common phenomenon observed in polymer electrolytes and can be explained as the result of weak ionic mobility since the degree of freedom of the ion transport is reduced as so much H_3PO_4 enters into the polymeric gel [13,14]. In addition, due to a lower dielectric constant of PEGDE ($\varepsilon_r < 8$), it can increase the ionic association at high H_3PO_4 concentration. Thus, the formation of ion-pairs and higher ion-multiples may occur in PEGDE and the associated species lowers the conductivity [15,16].

We noted that the polymeric gel membranes presented in this work all manifest the good mechanical properties and chemical stabilities even soaked in high H_3PO_4 concentrations. It was found that membrane samples tended to shrink when they are taken out from the aqueous acid solutions and dried naturally in the air for 1 day or long. Meantime, the color of the membranes changed from colorless transparent to yellow with increasing the H_3PO_4 content. Table 1 summarizes the amounts of H_3PO_4 uptake and water content after the immersion of the polymeric gel membrane in aqueous solutions with different concentrations of H_3PO_4. As mentioned above, the H_3PO_4 content depended not only on the acid concentration in the solution but also on the immersion time. In this table, the values obtained for the polymers immersed for 3 h are compared each other. When the dried membrane samples were re-introduced into their corresponding original acid solutions, both the membranes dimension and their specific conductivity soon recovered. And the yellow color of the membrane samples (which is a mark of the presence of free H_3PO_4 in the polymeric gel [12,17]) at high H_3PO_4 concentrations disappeared to recover their original colorless transparency again. This

Table 1
Gel composition of H_3PO_4-doped polymer complex (PEO-PMA/PEGDE/H_3PO_4)[a]

Concentration of H_3PO_4 (mol l^{-1})	Maximum H_3PO_4 uptake per gram of polymer (g)	Average of maximum water uptake per gram of polymer (g)	Color after drying
0.43	0.13		None
0.85	0.34		None
1.70	0.71	4.41	Yellowish
2.93	1.02		Yellowish
3.57	1.16		Yellowish
4.69	2.22		Yellowish

[a] Gel composition: PEO-PMA/PEGDE = 38/62 (in mass).

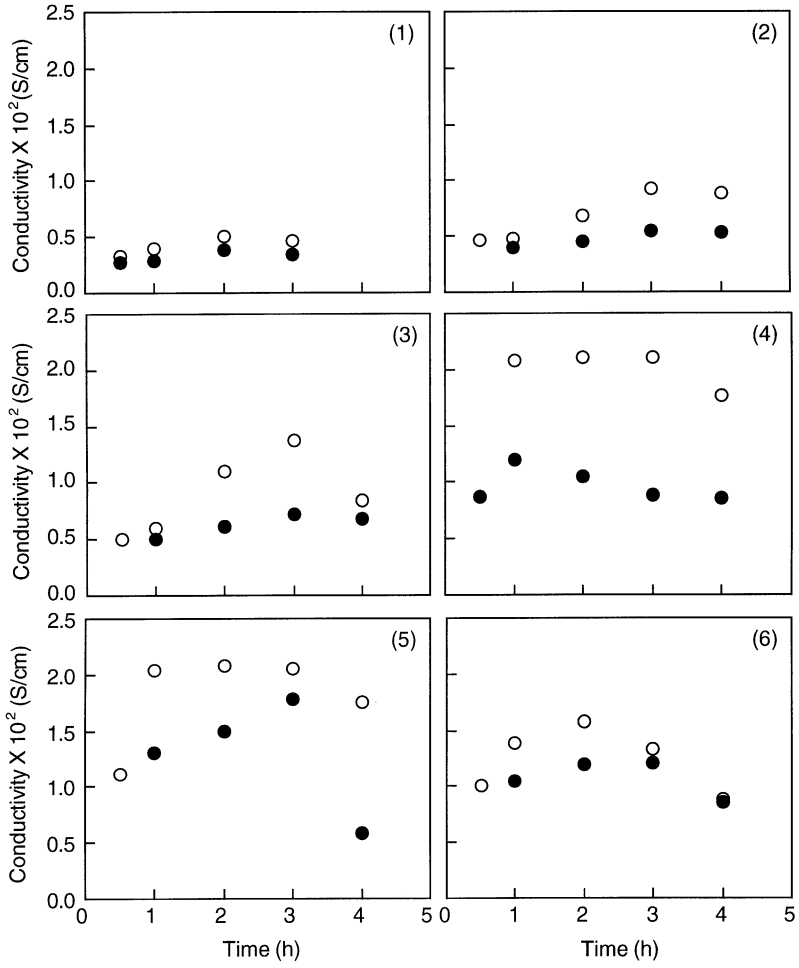


Fig. 3. Conductivity changes of gel electrolytes with immersion time under different H_3PO_4 concentrations (mol l^{-1}): (1) 0.43; (2) 0.85; (3)1.70; (4) 2.93; (5) 3.57; (6) 4.69. (●) PEO-PMA/PEGDE = 50/50 (in mass); (○) PEO-PMA/PEGDE = 38/62 (in mass).

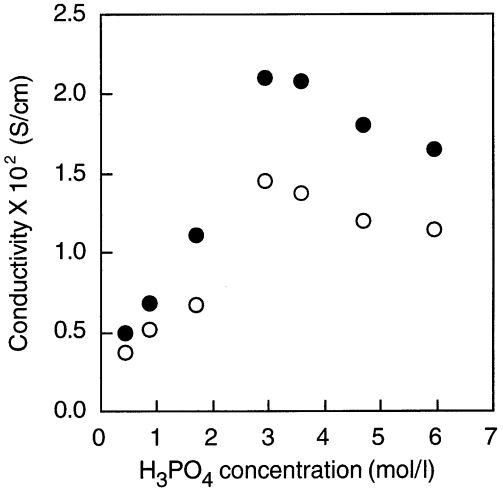


Fig. 4. Conductivity changes with the H_3PO_4 concentrations, at immersion time of 2 h. (○) PEO-PMA/PEGDE = 50:50 (in mass); (●) PEO-PMA/PEGDE = 38/62 (in mass).

observation also suggests that the proton conducting membranes developed in this study possess good reproducibility of conductivity and lifetime of usage.

The effect of the plasticizer content on the ionic conductivity is presented in Fig. 5, where the PEGDE content ranged from 38 to 65 mass%. A higher σ-value was observed for the membrane with higher PEGDE content. At the PEGDE content of 65%, the room temperature conductivity raises 6.3-fold as that at the lowest PEGDE content of 38%. Evidently, this can be attributed to an increase in the number of charge carriers due to PEGDE as the entrapped solvent. The low permittivity and protophilic nature of PEGDE allows it to promote the ion transport through the protonation by H_3PO_4. Thus, the higher the content of PEGDE, the higher the proton conductivity value was [13,18]. PEGDE was also noted to have a great influence on the mechanical stability of the polymeric gel membranes. It was found that the polymeric membranes became much brittle to broken easily when the content of PEGDE was lower than 35%, and very soft to be difficult in forming films and hard to handle as the PEGDE content was higher than 65%. Therefore, it can

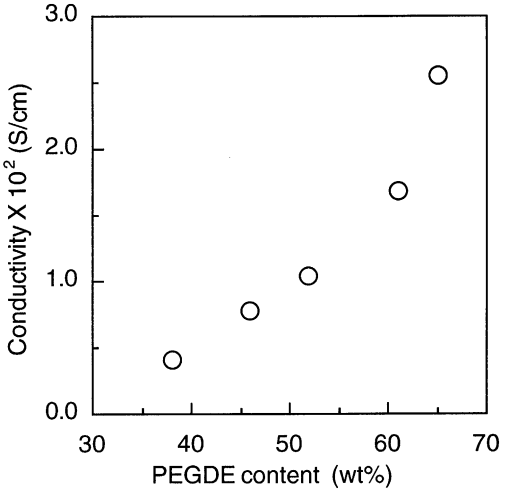


Fig. 5. Ionic conductivity at room temperature (25 °C) as a function of the plasticizer (PEGDE) content.

be concluded that PEGDE is both functioned as a plasticizer to stabilize the polymer membrane and as a complexing reagent to make a high σ-value. In this work, the ratio of 38/62 (in mass) of the matrix PEO-PMA to the plasticizer PEGDE was the optimum proportion both for obtaining high conductivity and good mechanical properties.

3.3. Temperature dependence of the conductivity

Fig. 6 shows the temperature dependence of the ionic conductivity for polymeric gel membranes with different H_3PO_4 concentrations. It can be seen that all the samples fitted well with Arrhenius relations when the H_3PO_4 concentration of the soaked solution was lower than 3 mol l^{-1}. The plot for the sample with low H_3PO_4 concentration

Table 2
Summary of the thermo-conductance analysis for PEO-PMA/PEGDE/H_3PO_4 complexes[a]

Concentration of H_3PO_4 (mol l^{-1})	T_{max} (°C)	σ_{max} (S cm^{-1})	E_a (kJ mol^{-1})
0.43	70	9.4×10^{-3}	6.7
0.85	70	9.8×10^{-3}	6.1
1.70	70	2.2×10^{-2}	4.1
2.93	70	2.8×10^{-2}	4.7
3.57	50	1.9×10^{-2}	–
4.69	30	2.2×10^{-2}	–

[a] Gel composition: PEO-PMA/PEGDE = 38/62 (in mass).

(0.43 mol l^{-1}) showed a light curvature. In Table 2, the maximum conductivity (σ_{max}) and the corresponding temperature (T_{max}) obtained for each H_3PO_4 concentration are summarized together with the apparent activation energy (E_a) for ionic conduction that were determined from the slopes of the Arrhenius plots. The maximum conductivity of 2.8×10^{-2} S cm^{-1} was obtained at 70 °C for the gel swollen with H_3PO_4 concentration of 2.93 mol l^{-1}. With the increase in the H_3PO_4 concentration, the activation energy for the conduction decreased gradually. This is in agreement with the fact that the density of ions in the gel increases with increasing the H_3PO_4 concentration (Table 1), thus the energy barrier to the proton transport decreases, which would lead to a decrease in the activation energy [19]. The values of the activation energy obtained from the Arrhenius plots were generally lower than 10 kJ mol^{-1}, which indicate that the proton transport mainly occurs via a Grotthus-type mechanism [20], in which the proton transport proceeds through the hydrogen bond. However, considering that the conductivity measured for the present system is much higher than that of the conventional polymeric gel

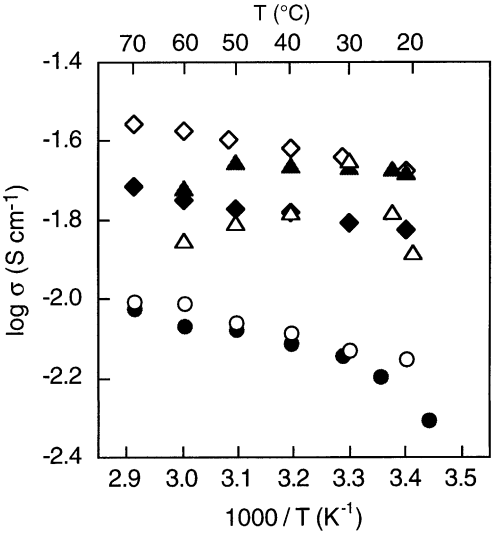


Fig. 6. Arrhenius plots for the ionic conductivity of PEO-PMA-based gel electrolytes. Gel composition: PEO-PMA/PEGDE = 38/62 (in mass); concentrations of H_3PO_4 (mol l^{-1}): (●) 0.43, (○) 0.85, (◆) 1.70, (◇) 2.93, (▼) 3.57, (▽) 4.63.

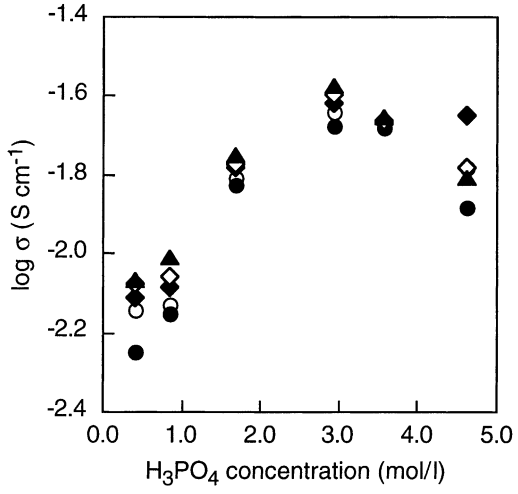
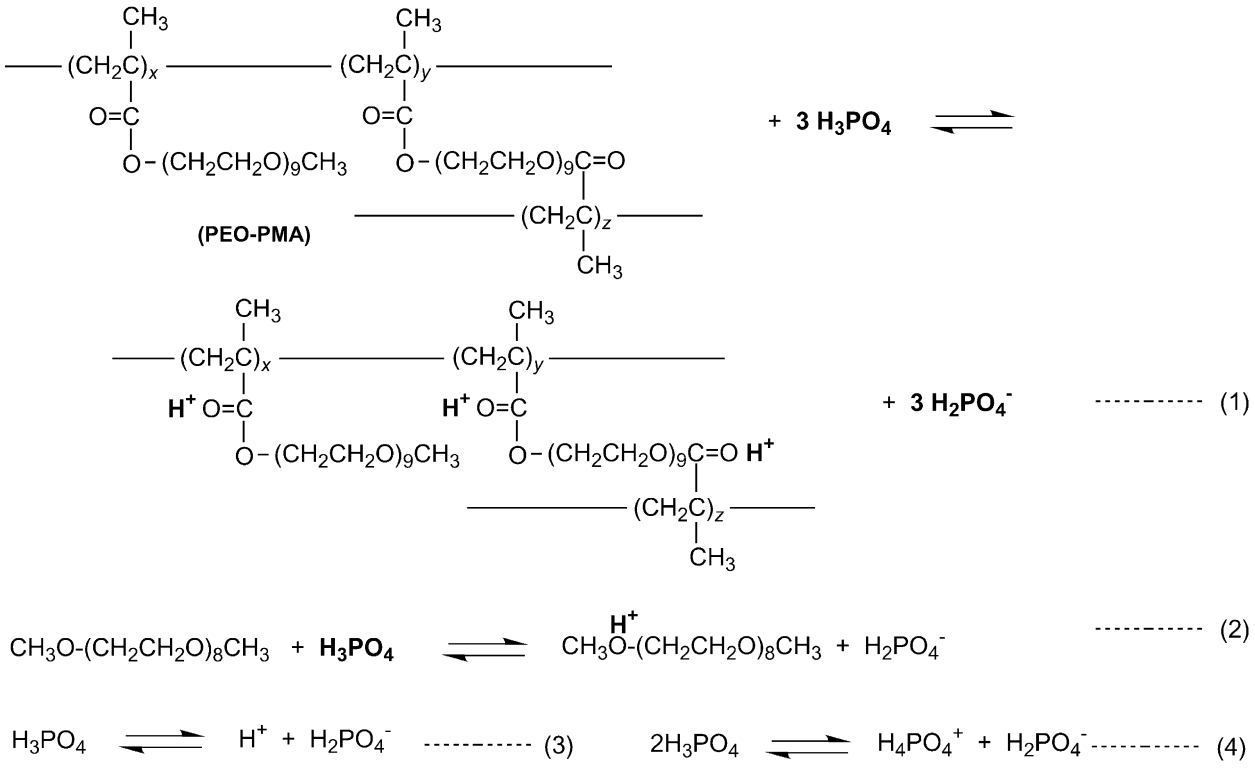


Fig. 7. Isotherms of the ionic conductivity of PEO-PAM/PEGDE/H_3PO_4-based gel electrolytes as a function of H_3PO_4 concentration in the solution. Gel composition: PEO-PMA/PEGDE = 38/62 (in mass); temperature (K): (●) 293, (○) 303, (◆) 313, (◇) 323, (▲) 333.



Scheme 1. Possible proton transport mechanisms in PEO-PMA/PEGDE/H_3PO_4 polymeric gel system.

systems [10,17,21,22], it is reasonable to assume that both Grotthus- and vehicle-type mechanisms [20,22] are possibly occur in the proton transportation process. The ionic motion in the present gel system seems to be highly decoupled from the segmental motion of the polymer matrix, thus the conductivity is rather close to that of a liquid electrolyte system [21]. However, when H_3PO_4 concentration was relatively high (3.57 and 4.69 mol l^{-1}), conductivity of the gel membrane does not follow the Arrhenius equation but showed an unusual non-linear conductivity response reaching a maximum around 40 or 50 °C. This anomalous behavior may be due to a specific interaction between the polymeric gel and H_3PO_4 resulting in an influence on the dissociation of H_3PO_4 or simple water loss at high temperatures [19,21].

Examination of the conductivity isotherms as a function of H_3PO_4 concentration is illustrated in Fig. 7. All the isotherms follow the same pattern with respect to the H_3PO_4 concentration. At each temperature, there is a tendency to pass through a maximum as the H_3PO_4 concentration is increased. This can be ascribed to the competing effects of increasing charge carrier density with increasing the ion-pairing and molecular associations reducing the ion mobility as well as the decrease in the segmental motion of the polymer [13–16].

It should be mentioned that the matrix itself also has the critical effects on either the concentration of the charge species or the ionic mobility in the resulting polymeric gel electrolyte. Since the PEO-PMA matrix has ether groups like PEGDE, which means that the polymer matrix is not an inert component. The PEO-PMA matrix can also act as a good proton acceptor and not provides a dimensional stability only, where the ions move through continuous conduction pathways provided by the solvent of PEGDE. Possible mechanisms for proton conduction in the present gel system are illustrated in Scheme 1. The PEO-PMA matrix is, in fact, plays a essential role to enclose the otherwise free phosphoric acid with a solid framework that provides a large number of charge carriers such as $H_2PO_4^-$ and even $H_4PO_4^+$. In addition, in the course of the sample preparation, the polymeric membranes were directly immersed in the aqueous H_3PO_4 solutions without washing the polymer membranes with any organic solvents. This would make an oligomeric PEO-PMA portion in the polymer exerted a significant plasticizing effect and an excess H_3PO_4 in the solid electrolytes, hence leading to a higher conductivity value [12,17].

4. Conclusion

Proton conducting polymeric gel membranes with high ionic conductivity and good mechanical properties were prepared by swelling the PEO-PMA polymeric gel with aqueous H_3PO_4 solutions. The ionic conductivity was dependent much on the concentration of H_3PO_4, the immersion time, and the plasticizer content. The optimum conditions were immersion time for 2–3 h, H_3PO_4 concentration

of 2.93 mol l^{-1} and the ratio of matrix to plasticizer around 40/60 (in mass) for obtaining both high proton conductivity and stability. Maximum conductivity of 2.6×10^{-2} S cm^{-1} was obtained at room temperature for the gel composition of the matrix to the plasticizier as 35/65 (in mass).

The proton conductivity gave a good Arrhenius relation in the temperature range of 20–70 °C, and the maximum conductivity of 2.8×10^{-2} S cm^{-1} was obtained at 70 °C for H_3PO_4 concentration of 2.93 mol l^{-1}, which is the highest proton conductivity for polymeric gel electrolyte systems reported so far. Both the Grotthus- and vehicle-type mechanisms exist in the conducting process for the present polymeric gel. FT-IR spectra showed that the high proton conductivity for present system is attributed to the presence of excess free H_3PO_4 in the polymeric gel in addition to the hydrogen-bonded H_3PO_4 to the polymer matrix.

Acknowledgements

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