

Polymeric Gel Electrolytes for Electric Double Layer Capacitors

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Abstract: Proton conducting polymeric gels as the electrolytes of electrochemical capacitors have been prepared by two different methods: 1) swelling a polymethacrylate-based polymer matrix in aqueous solutions of inorganic and organic acids, and 2) polymerizing complexes of anhydrous acids and prepolymers with organic plasticizer. The FT-IR spectra strongly suggest that the carbonyl groups in the polymer matrix interact with protons from the doped acids. High ionic (proton) conductivity in the range of 6×10^{-4} – 4×10^{-2} S cm⁻¹ was obtained at room temperature for the aqueous gels. The non-aqueous polymer complexes showed rather low ionic conductivity, but it was about 10^{-3} S cm⁻¹ at 70°C for the H₃PO₄ doped polymer electrolyte. The mechanisms of ion (proton) conduction in the polymeric systems are discussed.

Key words : Polymeric gel, Phosphoric acid, Ionic conductivity, Proton conduction, Electrochemical capacitor, Thermal stability

1. Introduction

Electric double layer capacitors (EDLCs) have been used as auxiliary power sources in portable electronics. They are also considered to be promising energy storage devices that can assist power plants using natural energy resources such as solar and wind, as well as fuel cells for electric vehicles (EVs). The present EDLCs consist of polarizable electrodes made of carbonaceous materials with high surface area and aqueous or non-aqueous electrolytes. Recently, some types of capacitors with organic solid electrolytes have been developed. We have also reported several types of polymeric gel electrolytes for EDLCs, and compared their capacitor performances with those with organic liquid electrolytes¹⁻⁴. In this paper, we describe proton-conducting polymeric gel electrolytes that have recently been developed^{5,6}. The solid proton conductor is applicable to so-called hybrid-type capacitors that consist of the double-layer electrode as activated carbon and pseudo-capacitance electrode as metal oxides⁷, because the charge-discharge reactions at both electrodes are accompanied by the proton exchange.

2. Experimental

The proton conducting polymeric gels were prepared by following two methods:

1) Polymethacrylate-based polymer matrix was first synthesized by photo-induced radical co-polymerization of poly(ethylene glycol) monomethacrylate and dimethacrylate (PEM, PED: Fig. 1) with proper amount of organic plasti-

cizer. The resulting polymer matrix was swollen with aqueous solutions of inorganic and organic acids². We used HCl, H₂SO₄, H₃PO₄, CH₃COOH (HAc), and (CH₂COO)₂H₂ (HSc) as the dopant. The polymeric gel contained dopant acids with a large amount of water. Thus, we can refer to this type of polymeric gel as "aqueous gel".

2) The dopant acids were directly mixed with the prepolymers, PEM and PED, together with the organic plasticizer, and then the resulting solution was hardened by the UV irradiation. The obtained polymeric film contained no water component. Thus, it will be called "non-aqueous gel". The organic plasticizers used in this work were poly(ethylene glycol) dimethylether (PEGDE), dimethylformamide (DMF), and propylene carbonate (PC).

The polymeric gels were characterized by spectroscopic techniques. FT-IR and X-ray diffraction (XRD) spectra were recorded at room temperature. The ionic conductivity was measured by an AC method in the temperature range from 20 to 70°C.

3. Results and Discussion

3.1. Aqueous gel

The chemical composition of the aqueous gel was varied with the preparation conditions. Figure 2 shows a typical result for the acid and water uptakes as a function of the acid concentration in the doping solution. Here the composition of the polymer matrix, the mass ratio of (PEO-PMA)/PEGDE, was 38/62. The acid (H₃PO₄) content in the gel increased with the concentration of the acid in the doping solution. On the other hand, the water uptake in the gel decreased with increasing the acid concentration in the solution. These

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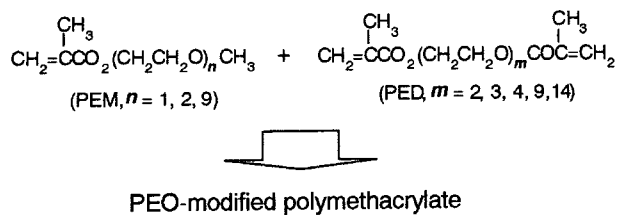


Fig. 1. Pre-polymers for matrix preparation.

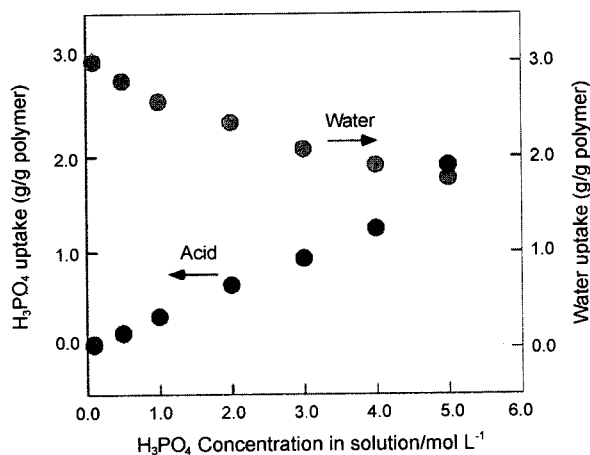


Fig. 2. Acid and water uptake in the polymeric gel.

trends were commonly observed for all acids examined.

Figure 3 shows FT-IR spectra obtained for the acid doped (PEO-PMA)/PEGDE (38/62 in mass). The original structure of the polymer matrix was kept after the acid doping. The broadening of the C=O band at 1730 cm^{-1} suggests that the doping of acids causes the protonation of carbonyl groups or strong molecular interaction between dopant acids and polymer matrix.

Figure 4 shows the variations of the ionic conductivity measured for the aqueous gels as a function of the acid concentration in the doping solution. In every gel system, the ionic conductivity once increased with the concentration of the acid in the solution, then decreased in the higher concentration region. This behavior is closely related to the profiles of the water and acid contents in the gel, as shown in Fig. 2. The higher the acid concentration in the doping solution results in the lower the water/acid ratio in the gel, which will be a cause of the decrease in the ionic conductivity of the gel. The highest conductivity was obtained for the gel containing H_2SO_4 or HCl doped from aqueous solution of about 1 mol dm^{-3} concentration. However, the conductance behavior was not so stable for the gels with such strong inorganic acids, especially at high temperature. The gels doped with organic acids, HAc and HSc, was thermally stable but showed rather low conductivity. Phosphoric acid was good dopant because it gave both high conductivity and good thermal stability of the gel. Fig. 5 shows the temperature dependence of the ionic conductivity for the aqueous gels containing difficult acids. The highest conductivity ($2.0 \times 10^{-2}\text{ S cm}^{-1}$ at 30°C

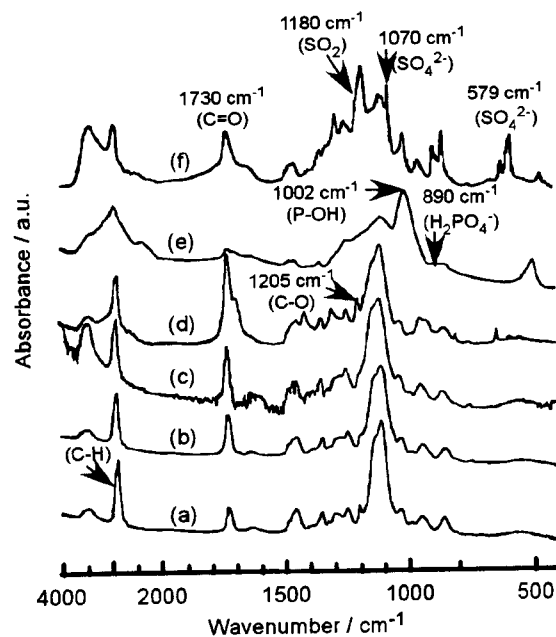


Fig. 3. FT-IR spectra of (a) (PEO-PMA)/PEGDE polymer matrix, (b) doped with HCl (2.0 mol dm^{-3}), (c) doped with HAc (3.0 mol dm^{-3}), (d) doped with HSc (0.5 mol dm^{-3}), (e) doped with H_3PO_4 (3.6 mol dm^{-3}), and (f) doped with H_2SO_4 (1.5 mol dm^{-3}). (PEO-PMA)/PEGDE = 38/62 (in mass).

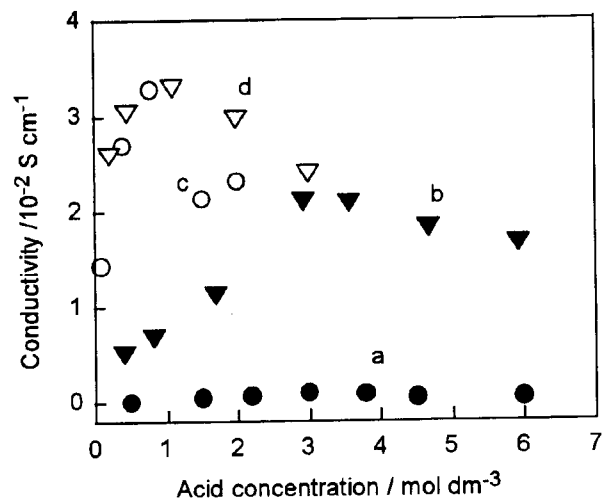


Fig. 4. Variations in the ionic conductivity of (PEO-PMA)/PEGDE-based gel film with acid concentration in the doping solution. Dopant: (a) HAc, (b) H_3PO_4 , (c) HCl, (d) H_2SO_4 . (PEO-PMA)/PEGDE = 38/62 (in mass).

and $2.8 \times 10^{-2}\text{ S cm}^{-1}$ at 70°C) was obtained for the aqueous gel of (PEO-PMA)/PEGDE/ H_3PO_4 doped from 3.0 mol dm^{-3} .

3.2. Non-aqueous gel

The radical polymerization of the mixture of PEM and PED containing H_3PO_4 /PEGDE (or PEGDE mixed with DMF) yielded a flexible transparent film with enough mechanical strength. Figure 6 shows XRD patterns for the (PEO-PMA)/PEGDE/ H_3PO_4 non-aqueous gels compared

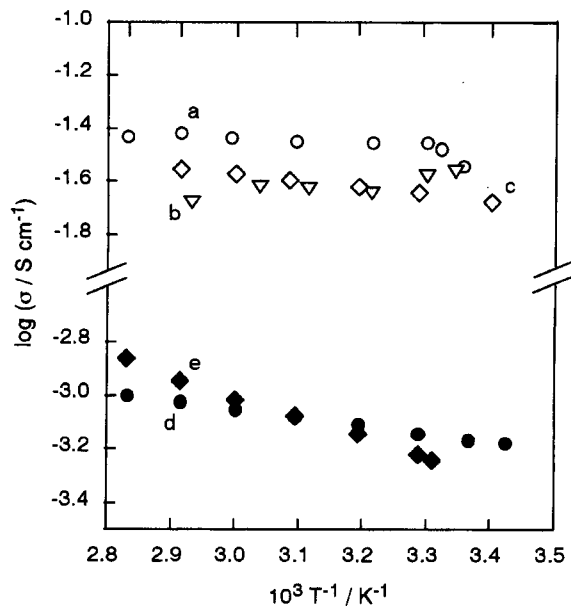


Fig. 5. Temperature dependence of the ionic conductivity for acid-doped (PEO-PMA)/PEGDE gel films. Acid and its concentration in the doping solution (mol dm⁻³): (a) H₂SO₄ (0.8), (b) HCl (0.2), (c) H₃PO₄ (2.9), (d) HAc (3.0), (e) HSc (0.5). Polymer composition (in mass): (PEO-PMA)/PEGDE = 38/62.

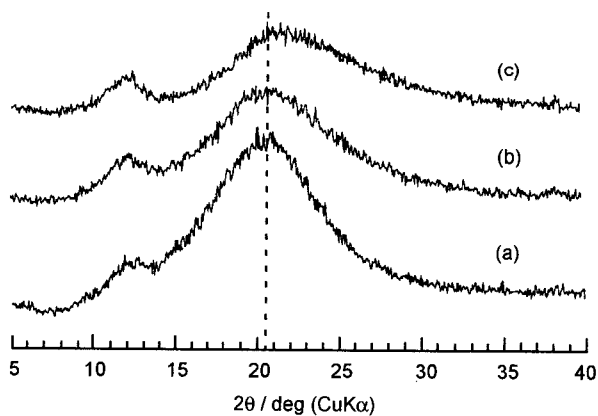


Fig. 6. XRD patterns for (PEO-PMA)/PEGDE/H₃PO₄ non-aqueous polymeric gels. H₃PO₄ content (in mass%):(a) 0, (b) 23 and (c) 46. (PEO-PMA)/PEGDE = 38/62 (in mass).

with that of the (PEO-PMA)/PEGDE polymer matrix. The broad diffraction peak centered at $2\theta = 20^\circ$ for (PEO-PMA)/PEGDE (curve a) is ascribed to a long-range ordered structure which is based on the repeated ethylene oxide (EO) units in the polymer matrix. The doping of H₃PO₄ caused broadening in the diffraction peak, and its extent depended on the acid content. The addition of DMF lead to further broadening, which suggests that the ordered structure of (PEO-PMA)/PEGDE is broken by the addition of DMF.

The thermal analysis of the (PEO-PMA)/PEGDE polymer matrix showed phase-transition (glass-transition) at around -100°C or below, depending on the matrix composition. Fig. 7 gives DSC profiles of the (PEO-PMA)/PEGDE/H₃PO₄ non-

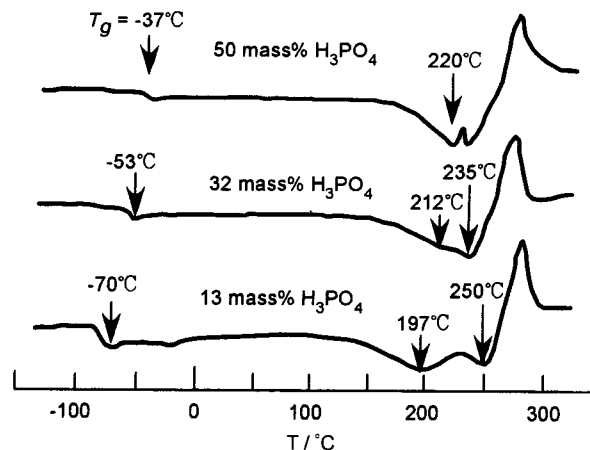


Fig. 7. DSC curves registered for (PEO-PMA)/PEGDE/H₃PO₄ gel electrolytes with different H₃PO₄ contents. (PEO-PMA)/PEGDE = 38/62 (in mass).

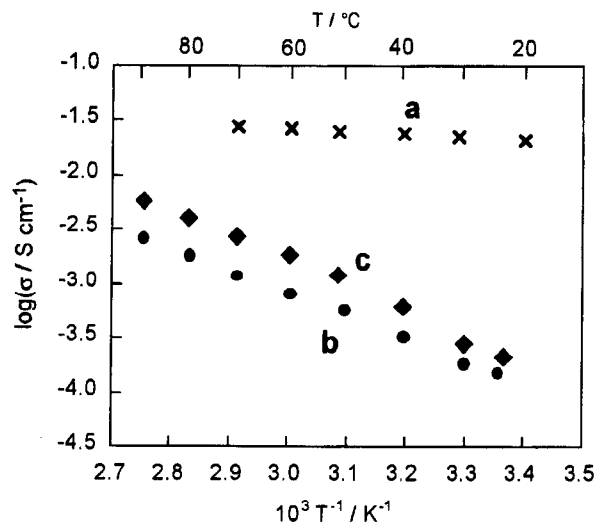


Fig. 8. Temperature dependence of the ionic conductivity for (PEO-PMA)/PEGDE/H₃PO₄ gel electrolytes. (a): (PEO-PMA)/PEGDE/H₃PO₄ (aqueous), (b): (PEO-PMA)/PEGDE/H₃PO₄ (nonaqueous), (c): (PEO-PMA)/PEGDE/DMF/H₃PO₄ (nonaqueous). [H₃PO₄ content: 46 mass% (b), 52 mass% (c)]

aqueous gels which were recorded under an ascending temperature condition of 10 K min^{-1} from -120°C to $+300^\circ\text{C}$ after a pre-heating/cooling cycle. The glass-transition temperature (T_g) was increased with the contents of H₃PO₄ in the gel. The endothermic responses prior to the thermal decomposition of H₃PO₄ around 280°C are probably due to partial evaporation of low molecular weight component in PEGDE. Thus, it can be concluded that the polymeric gel is thermally stable in a wide temperature range between -30°C to $+150^\circ\text{C}$.

Typical temperature dependences of the ionic conductivity for (PEO-PMA)/PEGDE/H₃PO₄ non-aqueous gels are shown in Fig. 8, where the data are compared by those obtained for an aqueous gel, (PEO-PMA)/PEGDE doped with aqueous H₃PO₄ solution. The ionic conductivity of the non-aqueous (PEO-PMA)/PEGDE/H₃PO₄ gel was lower than that of the

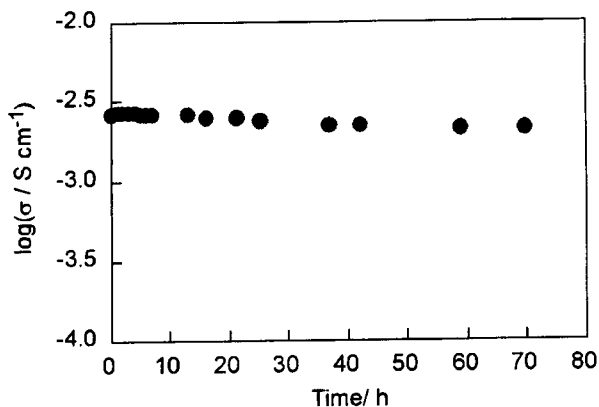


Fig. 9. Variation in the ionic conductivity of (PEO-PMA)/PEGDE/ H_3PO_4 with storage time at 100°C . H_3PO_4 content: 41 mass%, (PEO-PMA)/PEGDE = 38/62.

aqueous gel by two orders of magnitude at room temperature. At moderately high temperature ($>60^\circ\text{C}$), however, higher values than $10^{-3} \text{ S cm}^{-1}$ were observed. Addition of DMF as the plasticizer improved the ionic conductivity of the non-aqueous gel. Differences in the slope of the plots between the aqueous and non-aqueous gels, which correspond to the differences in the activation energy for the ionic conduction, suggest that the mechanism of the ion transport should be fairly different from each other. In the aqueous gel system, a conventional proton conduction mechanism similar to that in an aqueous solution was proposed, in which the process is accompanied by the exchange of the hydrogen bond through water molecules in the gel^{8,9}. In the non-aqueous system, on the other hand, direct hopping of proton should be feasible by the assistance of thermal motion of the repeated EO units in the polymer matrix, which is somewhat similar to those in the PEO complexes with alkali metal cations¹⁰.

Fig. 9 shows the variation of the ionic conductivity with time duration for the (PEO-PMA)/PEGDE/ H_3PO_4 non-aqueous gel at 100°C . The conductivity decreased slightly with duration time, but its change after 80 h standing was only about 5%. This suggests that the present (PEO-PMA)/PEGDE/ H_3PO_4 non-aqueous gel is practically stable, even under a moderately high temperature condition.

4. Conclusion

Two types of proton conducting polymeric gels have been prepared for the electrolytes of electrochemical devices. High ionic (proton) conductivity in the range from 10^{-4} to $10^{-2} \text{ S cm}^{-1}$ was obtained at room temperature for the aqueous gels. The non-aqueous polymer complexes with H_3PO_4 showed about $10^{-3} \text{ S cm}^{-1}$ of the conductivity at 70°C . The electrochemical characteristics of some electron-conducting materials were briefly examined using present aqueous and non-aqueous gels. Such transition-metal oxides as WO_3 showed high electroactivity as pseudo capacitor electrodes in the aqueous polymeric electrolyte. Details in the applicability of the present polymeric electrolytes for the capacitor devices are now under investigation.

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References

1. Y. Matsuda, M. Morita, M. Ishikawa, M. Ihara, *J. Electrochem. Soc.*, **140**, L109 (1993).
2. M. Ishikawa, M. Morita, M. Ihara, Y. Matsuda, *J. Electrochem. Soc.*, **141**, 1730 (1994).
3. M. Ishikawa, M. Ihara, M. Morita, Y. Matsuda, *Electrochim. Acta*, **40**, 2217 (1995).
4. M. Ishikawa, T. Kishino, N. Katada, M. Morita, *Mat. Res. Soc. Symp. Proc.*, **575**, 423 (2000).
5. J. L. Qiao, N. Yoshimoto, M. Ishikawa and M. Morita *J. Power Sources*, **105**, (2002).
6. J. L. Qiao, N. Yoshimoto, M. Ishikawa and M. Morita, *Electrochim. Acta*, **47**, 3441 (2002).
7. J. H. Park, O. O. Park, K. H. Shin, C. S. Jin, J. H. Kim, *Electrochem. Solid-State Lett.*, **5**, H7 (2002).
8. J. R. Stevens, W. Wiczorek, D. Raducha, K. R. Jeffrey, *Solid State Ionics*, **97**, 347 (1997).
9. G. Zukowska, N. Chojnacka, W. Wiczorek, *Chem. Mater.*, **12**, 3578 (2000).
10. M. Morita, T. Fukumasa, M. Motoda, H. Tsutsumi, Y. Matsuda, T. Takahashi, H. Ashitaka, *J. Electrochem. Soc.*, **137**, 3401 (1991).