

Novel Electrolyte System: Porous Polymeric Support Filled with Liquid Electrolyte

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SYNOPSIS

In this article, a novel electrolyte system composed of both porous polysulfone film and a propylene carbonate/LiClO₄ liquid solution occupying the pore is suggested. Porous polysulfone acts as a support which imparts a good mechanical property and accommodation of a liquid electrolyte. Using this approach, we could enhance the conductivity and mechanical property of the polymer electrolyte simultaneously. The maximum conductivity of this system was 3.93×10^{-3} S/cm at room temperature. The conductivity seems to be significantly affected by the amount of the uptake of the liquid electrolyte and also by the surface characteristics of the porous polysulfone. The path for ionic conduction is effectively formed with the increase in the uptake of the liquid electrolyte. Low-surface porosity and high-surface roughness is believed to reduce the ionic conduction. However, the denser surface layer of the support showed retarded evaporation of propylene carbonate under reduced pressure, indicating superior long-term stability. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Solid polymer electrolytes have attracted considerable attention because of their potential applications in batteries, fuel cells, chemical sensors, etc. Until now, studies have centered on increasing the ionic conductivity of the ion-polymer complexes with the aim of developing materials with commercial applications. Poly(ethylene oxide) (PEO) has been the favored solvating medium due to its ability to effectively coordinate with the salt cations and form homogeneous solutions.^{1,2} There are, however, several disadvantages to using such systems, the major one being that PEO tends to crystallize or forms crystalline complexes and acceptable levels of ionic conductivity can only be obtained above the melting temperature. Thus, studies have focused on decreasing the crystallinity and increasing the mechanical stability of the PEO-based electrolyte system.^{3,4} In spite of their efforts, the order of conductivity in the PEO-based systems did not exceed 10^{-4} S/cm.

Recently, room-temperature ionic conductivities on the order of 10^{-3} S/cm have been achieved by incorporating polar solvents and lithium salts into amorphous polymer matrix films.⁵⁻⁸ The polar solvents provide the medium for ionic transport, while the polymer matrix supports the mechanical strength. This approach is a more versatile alternative to the conventional approach which utilizes polymers that complex with metal salts. However, the amount of a polar solvent is limited by the reduction of mechanical strength, although the ionic conductivity increases with increasing the solvent content. For that reason, it is quite difficult for a plasticized polymer electrolyte system with an acceptable mechanical strength to show the high conductivity corresponding to that of the liquid electrolyte system.

In this article, we suggest a new electrolyte system which contains the liquid propylene carbonate (PC) phase and polymeric support, which is composed of interconnected micropores that are filled with a liquid PC/salt solution. The schematic features of such films are shown in Figure 1. The pores allow the conducting channel across the film. The microporous polysulfone acts only as a structural support and the channel filled with a liquid PC acts as a con-

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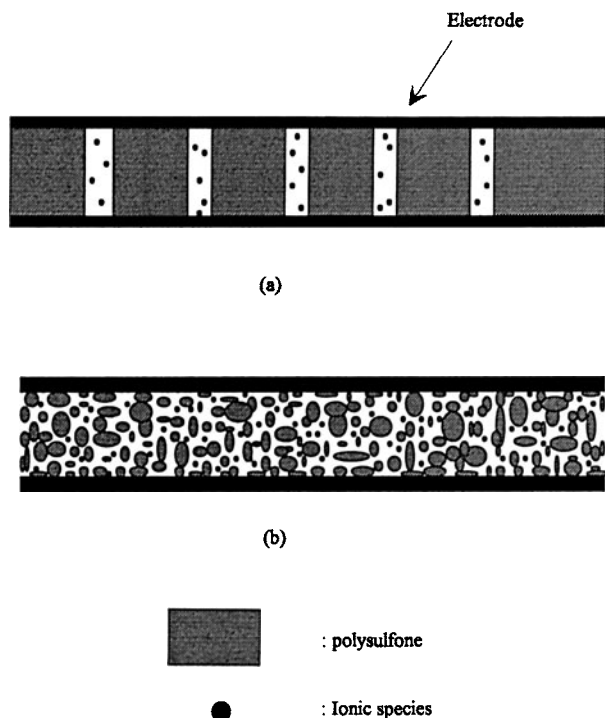


Figure 1 Schematic features of porous polysulfone support filled with liquid electrolyte: (a) large and well-developed macropores; (b) randomly connected micropores.

ducting pathway. The advantage obtainable from this approach is that the conductivity and mechanical property can be controlled independently by designing the structure of the polymeric support and by selecting the filled polar solvent properly.

The porous polysulfone was selected as a microporous support because of its good mechanical strength. The propylene carbonate was used as a pore-filled polar solvent due to its high boiling point which provides a long-term stability of the electrolyte cell. The ionic conductivities of the porous films with different morphology and various PC contents were investigated in this study.

EXPERIMENTAL

Sample Preparation

To prepare a porous polysulfone as a support in our electrolyte system, we used a phase-inversion method which is known to be effective for producing a porous structure. The *N*-methyl-2-pyrrolidone (NMP)/polysulfone solutions with the weight fractions of 85/15 and 90/10 were cast on the glass plate and then the solutions on the glass plates were

quickly immersed into a water bath to induce a phase inversion. The film was soaked in a water bath for 6 h to completely remove a residual NMP. To remove water that remained in the porous polysulfone film, we dried the films in a reduced pressure at 80°C for 1 day. The PC/LiClO₄ solution was filled in pores by immersing the porous polysulfone film in 6 wt % LiClO₄ in PC at 60°C for 1 week.

The amount of PC in the pores was varied by evaporating the PC in a vacuum at 30°C. The salt concentration of the PC/LiClO₄ solution in the pores was calculated from the initial concentration of the PC/salt solution and the weight loss during the evaporation. The amount of PC in the polymer electrolyte was expressed by the PC content ratio, which is defined as the ratio of the weight of filled PC to the maximum PC content. The maximum PC content was determined by the weight gain when the

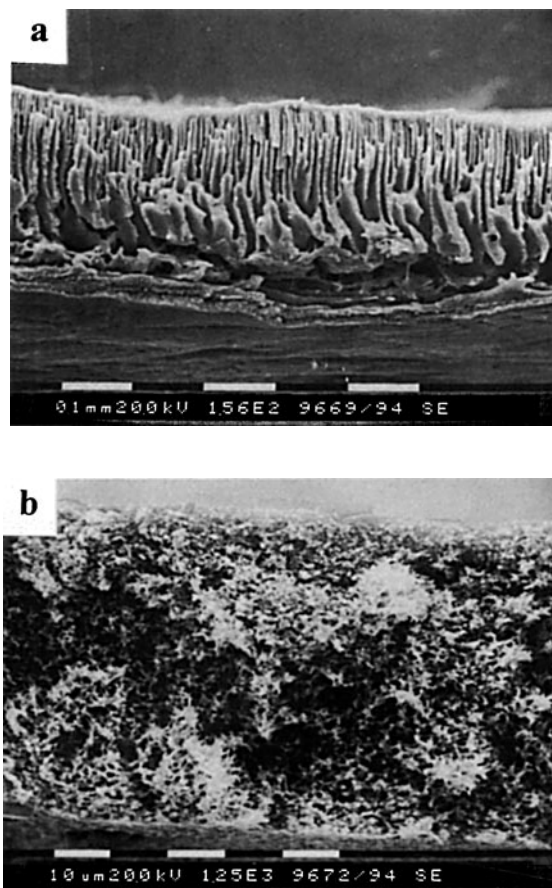


Figure 2 Micrographs of the cross sections of polysulfone support prepared from the two solution films, immersed into a pure water bath; weight ratio of NMP/polysulfone: (a) 85/15; (b) 90/10.

Table I The Conductivities of the Porous Polysulfone Support Filled with Liquid Electrolyte

psf1 ^a			psf2 ^b			psf3 ^b		
PC Content Ratio	Salt Concentration (Wt %)	Conductivity ($\times 10^4$) ^c	PC Content Ratio	Salt Concentration (Wt %)	Conductivity ($\times 10^4$) ^c	PC Content Ratio	Salt Concentration (Wt %)	Conductivity ($\times 10^4$) ^c
1.0	6.0	3.9	1.0	6.0	—	1.0	6.0	39.3
0.99	6.3	2.0	0.96	6.8	7.3	0.86	7.0	20.0
0.97	6.7	1.7	0.91	7.9	6.0	0.78	7.7	13.8
0.96	6.8	1.6	0.89	8.2	4.7	0.70	8.6	7.79
0.95	7.0	1.3	0.86	8.8	4.1	0.62	9.7	7.70
0.94	7.3	0.9	0.84	9.4	3.6	0.56	10.6	7.28
0.91	7.8	0.97	0.82	9.9	1.7	0.51	11.8	5.67
0.90	8.2	0.86	0.78	10.8	1.0	0.41	14.8	5.46
0.89	8.4	0.66	0.73	12.3	0.1	0.25	24.3	3.16

^a NMP/psf = 85/15 (wt fraction). Swelling in 6% PC/LiClO₄ solution.

^b NMP/psf = 90/10 (wt fraction). Swelling in 6% PC/LiClO₄ solution.

^c Unit = [S/cm].

porous polysulfone was immersed for 1 week at 60°C and the PC at the surface was removed.

Electron Microscopy

The morphologies of the polysulfone supports were investigated by using a scanning electron microscope (Phillips SEM 535M). Specimens for the SEM image of the broken side were prepared in liquid nitrogen.

Impedance Measurement

The electrical properties of the polymer electrolyte films were measured by ac impedance spectroscopy at frequencies ranging from 100 to 10⁷ Hz, using a system based on a Solartron SI1255 frequency response analyzer. The planar stainless steel was used as electrodes. All the impedance measurements were performed at room temperature. The area of the electrode was 1.13 cm².

Viscosity Measurement

The relative viscosity in this study is defined as the viscosity ratio of the PC/LiClO₄ solution to the pure PC. It is generally approximated with the elution time ratio which is measured by using a Cannon-Fenske-type viscometer at 25°C.

RESULTS AND DISCUSSION

To confirm that the porous polysulfone support is not associated with ionic conduction, the conduc-

tivity of nonporous polysulfone film swollen with the PC/lithium perchlorate solution was tested. The weight percentage of PC/salt solution in swollen polysulfone at 60°C was 34 wt %. Its conductivity was so low that its resistance exceeded the detection limit of our impedance spectrometer. This result indicates that the ionic conduction through the polysulfone matrix can be neglected in our system.

We prepared two porous polysulfone supports of which microstructures were similar to the schematic features shown in Figure 1 (a) and (b). The support psf1 was prepared from the 85/15 NMP/polysulfone solution, and the support psf2, from the 90/10 solution. The SEM images of their cross sections are given in Figure 2 (a) and (b), respectively. The large and well-developed macropores were found in psf1, while the randomly connected micropores were observed in psf2. These structural differences of the polysulfone supports result from the difference of the composition of the casting solution.^{9,10} When the casting solution is dilute, the penetration rate of water through the cast polymer solution is high, resulting in fast phase inversion. For psf2, the fast penetration of water molecules leads to small and three-dimensionally interconnected micropores. Contrary to psf2, the large macropores were developed in psf1 due to the slow diffusion of water molecules from the skin layer during the phase inversion. The slow penetration of water caused the growth of the macrovoid. A more detailed mechanism on pore formation can be found elsewhere.^{11,12}

We confirmed that the porous structures of these polysulfone supports were retained, when the PC/salt solution was filled, by investigating the SEM image of the polysulfone support. When these pores

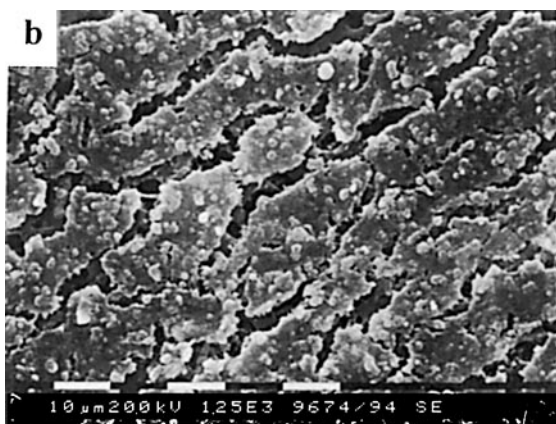


Figure 3 Micrographs of the surface of polysulfone support prepared from the two solution films, immersed into a pure water bath; weight ratio of NMP/polysulfone: (a) 85/15; (b) 90/10.

were filled with liquid PC/salt solution, high conductivities were obtained on both polymer electrolytes. The maximum conductivity obtained in our work was 3.93×10^{-3} S/cm, as shown in Table I. These results evidently indicate that the open pores filled with the liquid PC/salt solution provide the conducting pathways for ionic conduction. Ions in the PC/salt solution flow toward the electrode through each conduction channel when the channels are filled with PC solution and the conduction path is connected from the one electrode to the opposite one.

The structural difference between psf1 and psf2 was considered to investigate the effect of the dimension and tortuosity of the conduction pathway on the conductivity. These porous polysulfone supports have structural inhomogeneity. Since polysulfone in NMP solution abruptly coagulated and

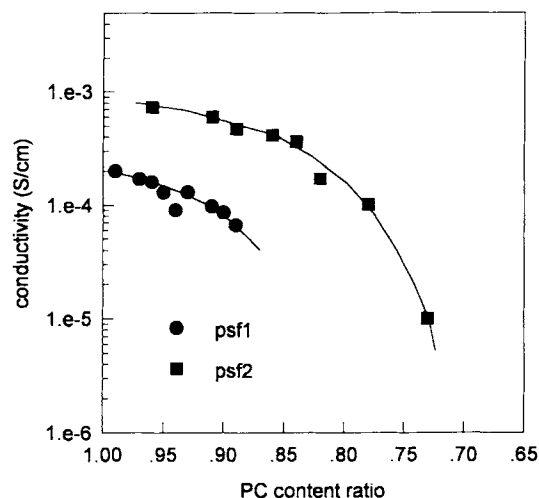


Figure 4 The change of conductivity with a PC content in the pores; dried in a vacuum oven at 30°C.

became immobile at their interface when the casting solution contacts with water, the dense skin layer is produced at the top and bottom of the film. Due to the formation of the dense skin layer, the penetration of water through the polymer solution is retarded, resulting in slow phase inversion and, consequently, the large pores are developed in the interior of the polysulfone support.^{11,12} Therefore, more porous morphology was generated at the interior rather than at the surface of the film. Since the surface and interior of the film have different morphology, the surface characteristic of the film should be also considered as well as the interior of the film where the conducting channel is developed.

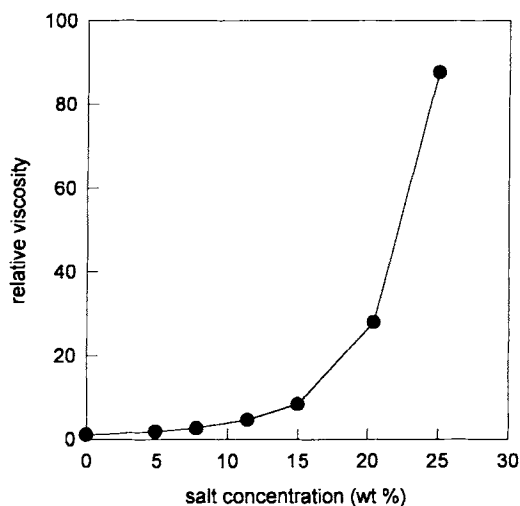


Figure 5 The relative viscosity change of the PC/LiClO₄ solution with a salt concentration at 25°C.

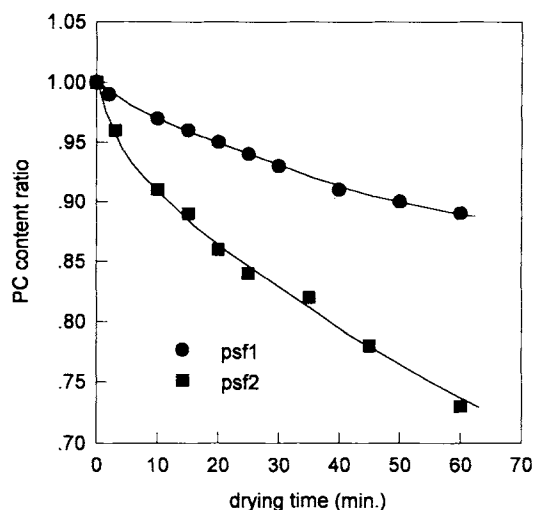


Figure 6 The change of PC content with drying time; dried in a vacuum oven at 30°C.

Figure 3 shows the SEM image of the surface of psf1 and psf2. One can see that psf1 has smaller pores and fewer surface pores than has psf2. These differences also resulted from the concentration difference of the casting solution.^{9,10} The higher initial polymer concentration in the casting solution can result in a denser surface layer. Although the larger pores were produced in psf1 in the interior, its surface layer was denser and thicker than that of psf2. From the viewpoint of the size of the pore and tortuosity of the conducting path across the polymeric support, psf1 is expected to show faster ionic transport than that of psf2, because the conduction pathway is less tortuous. On the other hand, the denser and less porous surface layer can act as an additional resistance to the ionic conduction. We investigated the conductivity of the two polymer electrolyte films considering the above two morphological characteristics.

The maximum wt % of the PC when it is filled in the pores was found to be 70 and 69 for psf1 and psf2, respectively. The conductivities of psf2 were higher than those of psf1 for all the PC content ratios, as shown in Figure 4 and Table I. This fact strongly indicates that the morphological character of the surface layer governs the ionic transport rate rather than that of the interior. It is believed that the ionic conduction is limited at the surface layer. The higher conductivity can thus be obtained by increasing the porosity of the surface layer.

Figure 4 reveals the change of the conductivity with the PC content ratio. The conductivity decreases with decreasing PC content ratio for both polymer electrolyte films. For psf2, the conductivity

was decreased from 7×10^{-4} to 1×10^{-5} , when 30 wt % of PC was evaporated. The decrease of the conductivity can result from two factors: One could be the relative viscosity change of a PC solution in pores as the PC evaporates. The initial salt concentration in pore-filled PC/salt solution was 6 wt %. When 30% of the filled PC was evaporated, the salt concentration increased to 12 wt %. Figure 5 shows the change of the viscosity with increasing salt concentration. It should be noted that the viscosity is doubled as the concentration is changed from 6 to 12 wt %, but the 70-fold decrease of the conductivity can hardly result from only the twofold increase of the viscosity. The more important factor would be the increase of the vacant space in the pores at the interface between the electrode and the film. As the PC evaporates, the volume of PC filled in the pores decreases and the ionic conduction is limited by the vacant space of the pores.

One of the disadvantages of this system as well as a plasticized polymer electrolyte system is the evaporation of the solvent, which results in decrease of the conductivity. Thus, prohibition of the evaporation of a polar solvent is required for long-term stability.

Figure 6 represents the changes of the PC content with drying time. The PC content was varied by evaporating the PC under vacuum at 30°C. psf2, having a more porous surface layer, showed faster removal of the PC than did psf1 upon drying. For psf1, the dense surface layer seems to act as a resistant layer for solvent evaporation. This result suggests that the polymer electrolyte film having a dense surface layer would be adequate for long-term use, although it restricts the ionic conduction.

Since the pore filled with liquid electrolyte provides the ionic conduction pathway, the uptake of the liquid electrolyte is very important for effective ionic conduction. To clearly show the importance of the amount of the uptake on the ionic conductivity, the ionic conductivities of the two electrolyte membranes, psf2 and psf3, were compared. psf2 and the psf3 have the same morphology since both were prepared from the 90/10 NMP/polysulfone solution. They are only different in the amount of the liquid electrolyte filled in the pore. The weight percentages of the filled liquid electrolyte in psf2 and the psf3 were 69 and 87 wt %, respectively; the amount of the liquid electrolyte in psf3 was three times larger than that of psf2. Their conductivities were 7.3×10^{-4} S/cm for psf2 and 3.93×10^{-3} S/cm for psf3 as given Table I, which shows that the path for ionic conduction could be more effectively

formed if the higher fractions of the pores are occupied with liquid electrolyte.

This new and simple polymer electrolyte system suggests that it can be one of the candidates for commercial electrolytes. As previously described, the characteristics of the skin layer seems to be important for performance. The denser surface character leads to lower conductivity but makes a more enhanced retardation of PC evaporation. The fine tuning of the two requirements and the improvement of surface contact should be studied extensively in this system. The amount of the uptake of the liquid electrolyte is important to produce an effective ionic conduction pathway, and, thus, further works should be also concentrated on the increase of the uptake for the enhancement of the ionic conductivity.

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