Gel Polymer Electrolytes Prepared with Porous Membranes Based on an Acrylonitrile/Methyl Methacrylate Copolymer

HYO-SIK MIN,[1] DONG-WAN KANG,[1] DOO-YEON LEE,[2] DONG-WON KIM[1]

[1] Department of Chemical Technology, Hanbat National University, San 16-1, Dukmyung-Dong, Yusung-Gu, Taejon 305-719, South Korea

[2] Materials and Devices Sector, Samsung Advanced Institute of Technology, Suwon 440-600, South Korea

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ABSTRACT: Porous membranes based on acrylonitrile/methyl methacrylate copolymer were prepared by a phase-inversion method. Microstructures of the porous membranes were controlled through the variation of the evaporation drying time before immersion in a nonsolvent bath. Gel polymer electrolytes were prepared from these porous membranes via soaking in an organic electrolyte solution. They encapsulated the electrolyte solution well without solvent leakage and maintained good mechanical properties that allowed the preparation of thin films (~23 μm). These systems showed acceptable ionic conductivity values ($>6.0 \times 10^{-4}$ S/cm) at room temperature and sufficient electrochemical stability over 4.4 V that allowed applications in lithium-ion polymer batteries.
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INTRODUCTION

A large number of studies have been carried out on rechargeable lithium polymer batteries with gel polymer electrolytes in which the liquid electrolyte has been immobilized by incorporation into a matrix polymer, such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate) (PMMA), poly(vinyl chloride), and poly(ethylene oxide).[1–7] Although these gel polymer electrolytes exhibit high ionic conductivities exceeding 10^{-3} S/cm, most of them have various deficiencies preventing them from being used in commercial lithium batteries. Most of the processes for preparing gel polymer electrolytes require a moisture-free environment because of the higher water sensitivity of the lithium salt. Furthermore, their mechanical properties are often very poor, and the films have to be hardened by either chemical or physical curing. To overcome these difficulties, researchers have investigated an activation process in which a porous polymer film is soaked in an electrolyte solution.[8–12] Unlike conventional methods such as solution casting and direct dissolution of the polymer in the electrolyte solution, this procedure requires critical moisture control only during the last activation step. Of the various polymers that can be used for this purpose, PVdF and its copolymers have mostly been studied because the electrolytes prepared with these polymers satisfy most of the properties required for battery applications. However, gel polymer electrolytes based on porous PAN membranes have received little attention, although PAN has been used in preparing gel

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Correspondence to: D.-W. Kim (E-mail: dwkim@hanbat.ac.kr)

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polymer electrolytes by direct dissolution of the host polymer in the electrolyte.

In this study, we prepared highly conductive porous polymer electrolytes by using an acrylonitrile (AN)/methyl methacrylate (MMA) copolymer as the preferred matrix polymer. MMA is useful as a comonomer because of its ability to be easily wetted by polar solvents. The porous membrane is prepared by a phase-inversion method, which has been shown to be effective for producing porous structures.[13] Gel polymer electrolytes are prepared by the soaking of the porous membranes in electrolyte solutions. The electrochemical characteristics of these gel polymer electrolytes will be reported.

EXPERIMENTAL

Polymer Synthesis and Characterization

The copolymer used in this work, consisting of AN and MMA (hereafter called the AM copolymer), was synthesized via emulsion polymerization with distilled water at 60 °C in a glass reactor equipped with a nitrogen inlet, a reflux condenser, an addition funnel, and a mechanical stirrer. Potassium persulfate ($K_2S_2O_8$) was used as a free-radical, water-soluble initiator, and sodium lauryl sulfate was used as an emulsifier. The polymerization was continued for 5 h with vigorous agitation. The polymer was isolated by filtration and washed with distilled water at 80 °C for the removal of any impurities such as residual monomers and initiator. The product was then dried in a vacuum oven at 80 °C for 24 h. A white powder was obtained as the final product. ^{1}H NMR spectra were obtained in dimethyl sulfoxide-d_6 with a Bruker DRX-300 NMR spectrometer with tetramethylsilane as an internal standard reference.

Preparation of the Membranes

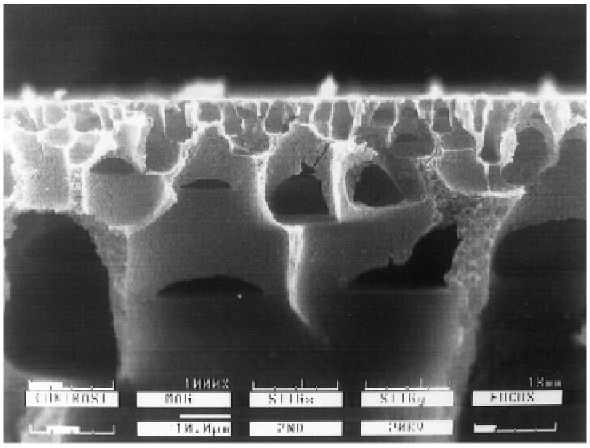
The AM copolymer was dissolved at a concentration of 5 wt % in dimethylformamide (DMF). After complete dissolution, the resulting viscous solution was cast with a doctor blade onto a glass plate and then left to stand for 0–20 h with a time interval of 5 h so that some of the solvent could evaporate. Changing the drying time controlled the amount of DMF in the cast film. After evaporation at room temperature for different lengths of time, the films were immersed in a water bath for 6 h to induce phase inversion. After the exchange of DMF and water by phase inversion, a substantial number of pores were formed in the films. The resulting membranes were washed with running water and immersed again in a pool of deionized water for 24 h. The membrane was then vacuum-dried at 40 °C for 24 h. Dried membranes were obtained, the thicknesses of which varied from 22 to 117 μm, depending on the drying time of the casting solution. The water content in the membranes was less than 50 ppm. The morphology of the porous membranes was examined with a JEOL JSM-6300 scanning electron microscope. Cross-sectional views of the membranes were obtained by the membrane being broken in liquid nitrogen. The density of the membranes was measured by a standard pycnometric method.

Electrical Measurements

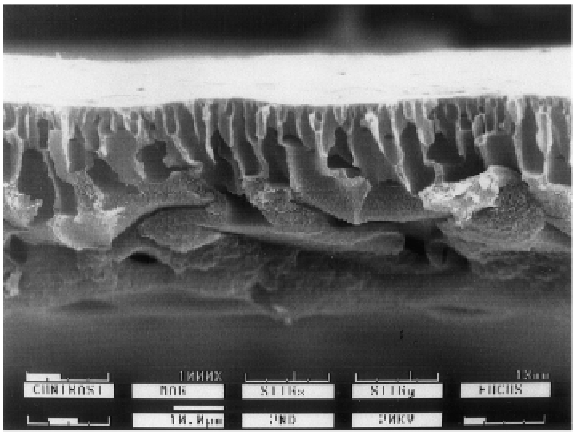
The dried membranes were transferred into a glove box and soaked in 1.0 M $LiPF_6$ or 1.0 M $LiBF_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v, battery-grade; Samsung Cheil Industries) for 3 h for activation of the porous membrane. The wetted membrane was cut into 4-cm^2 pieces and was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The cell was enclosed in an aluminum plastic pouch and sealed for testing outside of a glove box. The alternating-current impedance measurements were performed with a Zahner Elektrik IM6 impedance analyzer over a frequency range of 10 Hz to 100 kHz. Linear sweep voltammetry was performed with an SS working electrode, with counter and reference electrodes of lithium, at a scan rate of 1.0 mV/s. All cell assemblies were carried out in a drybox filled with argon gas.

RESULTS AND DISCUSSION

In our previous study, gel polymer electrolytes based on AM copolymers with a low content of AN ($AN < 56$ mol %) were prepared by a solution-casting method, and their electrical properties were reported.[14] In this work, attempts were initially made to prepare porous membranes from these copolymers. However, the uptake of polar solvents during activation resulted in the dissolution of these copolymers with low AN contents. Therefore, we tried to prepare porous membranes from AM copolymers with higher contents of AN.



(a)



(b)

Figure 1. SEM images of cross sections of the porous membranes prepared by the phase-inversion method: (a) immersion in a water bath without any evaporation step and (b) immersion in a water bath after evaporation of the solvent for 10 h.

The molar composition of the AM copolymer synthesized in this work was determined by the ^{1}H NMR spectrum, as previously described.[14] The molar composition of AN and MMA in the copolymer synthesized was calculated to be 84:16. The AM copolymer with 84 mol % AN did not dissolve in electrolyte solutions such as $LiPF_6$–EC/DMC.

Figure 1 shows scanning electron microscopy (SEM) images of cross sections of porous AM copolymer membranes. The porous membranes were obtained by immersion in a water bath after evaporation of the solvent for 0 and 10 h, respectively. During evaporation of the casting solvent, some phase separation was observed before immersion in water, which means that the phase separation was time-dependent. Both membranes exhibited a large number of short, fingerlike cavities beneath the upper layer. The pore size increased from the top to the bottom of the membrane. In the phase-inversion process, the membrane is formed by polymer precipitation, which occurs as a result of concentration variations following diffusive interchange between the solvent (DMF) and nonsolvent (water). Because the copolymers in solution abruptly coagulated and became immobile at the upper layer when the casting solution came into contact with the water, an upper skin layer was produced at the top of the membrane. This top layer should form at very short times and, consequently, can act as a barrier against subsequent interdiffusion of the solvent and nonsolvent. The top layer was quite compact; this means that the hole density was low. The retardation of water penetration resulted in a slowing of the phase-inversion process, and so larger cavities developed in the bottom of the membrane, which was in contact with the glass plate. An increase in the polymer concentration in the casting solution with increasing evaporation time led to the formation of a less porous membrane, as shown in Figure 1(b). It was characterized by pore size distributions of 0.5–4.0 μm. Increasing the evaporation time gave a much higher polymer concentration. This implies that the volume fraction of the polymer increased, and so a less porous membrane was obtained. These results suggest that both the pore size and pore volume could be controlled by changes in the evaporation time of the solvent before immersion in a nonsolvent bath, which affects the uptake of the electrolyte solution during the activation step, which is discussed in detail later.

We investigated the physical properties of the porous membranes with different microstructures, and the results are given in Table 1. The porosity of the membrane (φ) was determined with the following equation:[10,15]

$$\varphi = 1 - \rho_m/\rho_p$$

where ρ_m and ρ_p are the apparent density of the porous membrane and the density of the AM copolymer, respectively. An increase in the evaporation time led to the formation of a thinner membrane because the solvent in the casting solution slowly evaporated during the drying period. A decrease in

Table 1. Physical Properties of Porous Membranes Prepared by Changes in the Evaporation Time

Evaporation Time (h)	Thickness (μm)	Density (g/cm^3)	Porosity	Electrolyte Uptake (%)	Ionic Conductivity (S/cm)
0	117	0.092	0.92	95	1.4×10^{-3}
5	45	0.187	0.84	91	1.0×10^{-3}
10	23	0.731	0.37	66	6.4×10^{-4}
15	22	0.742	0.36	57	5.1×10^{-4}
20	22	0.744	0.36	56	4.6×10^{-4}

the membrane thickness resulted in an increase in the apparent density of the membrane; this means the formation of less porous membranes. These results are consistent with the SEM images shown in Figure 1: an increase in the evaporation time led to the formation of a denser membrane with a smaller pore volume. However, it should be noted that further evaporation of the solvent after 10 h had little effect on the thickness and porosity of the membrane. The solvent in the casting solution gradually evaporated from the upper surface of the membrane in contact with air. A dense surface layer was produced because of the solvent evaporation during the initial drying period. The dense surface layer formed at times of less than about 10 h might have prohibited the continual evaporation of the solvent from the interior of the casting solution because the volatility of the solvent was not so good. That led to the formation of a membrane with a similar microstructure after phase inversion in water, even if the casting solution was further dried over 10 h. The uptake of the electrolyte solution and ionic conductivity data after the soaking of porous membranes in $LiPF_6$–EC/DMC are also given in Table 1. The uptake of the electrolyte solution into the porous membranes resulted in swelling or gelation of the copolymer, rather than dissolution. It is well known that PAN is not soluble in organic solvents such as EC and DMC at room temperature. However, PMMA is easily dissolved in these organic solvents. A high AN content in the AM copolymer (84 mol % AN) would contribute to the mechanical stability of the membrane after the soaking of the porous membranes in the electrolyte solution. The uptake was calculated by the consideration of the amount of the electrolyte solution absorbed by the porous membrane as follows:

$$\text{Uptake }(\%) = (W_w - W_d)/W_w \times 100$$

where W_w and W_d are the weights of the wet and dry membranes, respectively. From the data in Table 1, it can be seen that an increase in porosity enabled the porous membranes to absorb more electrolyte solution; this suggests that the existence of pores in the membrane enhanced the absorbability of the membrane for the electrolyte solution. Gel polymer electrolytes prepared with membranes of 92% porosity showed the highest ionic conductivity. However, they were sticky and difficult to handle because the membranes with higher porosity easily swelled by imbibing organic solvents. However, a decrease in the electrolyte uptake for the membrane with lower porosity led to the formation of a gel polymer electrolyte with low ionic conductivity and good mechanical stability. Among the membrane systems studied in this work, the gel polymer electrolyte prepared with membranes of 37% porosity had the best combination of characteristics, namely, acceptable ionic conductivity and good mechanical strength. In the following, we report on the characterization of the gel polymer electrolytes prepared with membranes of 37% porosity.

Figure 2 shows an Arrhenius plot of ionic conductivities for gel polymer electrolytes prepared by the soaking of porous membranes in different electrolyte solutions. The temperature dependence of the $LiBF_4$-based gel polymer electrolyte was different from that of the $LiPF_6$-based one. For the gel polymer electrolyte prepared with $LiBF_4$–EC/DMC, the ionic conductivity was lower than that of the gel polymer electrolyte prepared with $LiPF_6$–EC/DMC for all temperatures, and its ionic conductivity abruptly decreased at a low temperature. It is well known that an abrupt decrease in ionic conductivity is observed at low temperatures when easily freezing solvents are employed in preparing gel polymer electrolytes.[2] It can be thought that the affinity of porous membranes for electrolyte solutions affects the low-temperature conductivity because the crystallization tendency of a solvent is associated with the polymer–solvent interactions. Although a de-

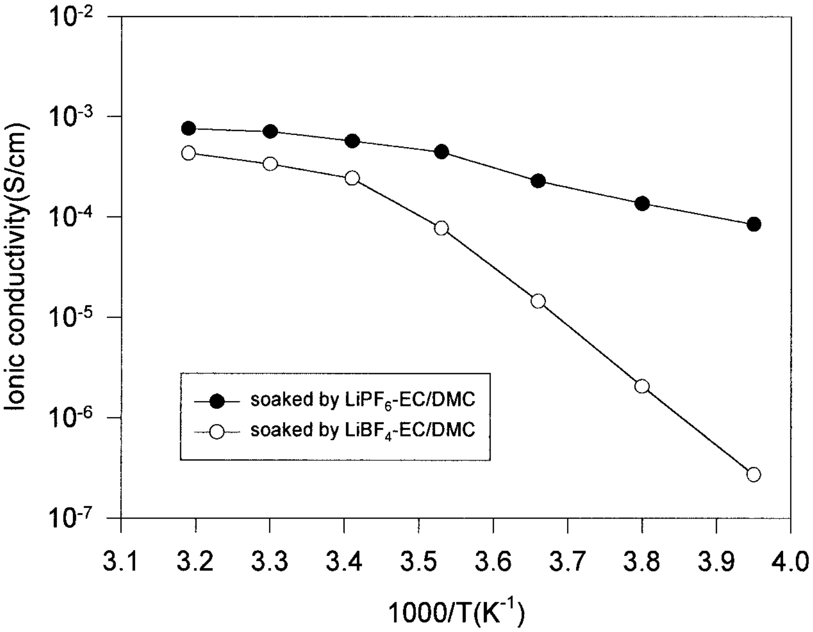


Figure 2. Temperature dependence of the ionic conductivity for gel polymer electrolytes prepared in different electrolyte solutions.

tailed study of the phase diagram of the components in the gel polymer electrolyte is beyond the scope of this article, we tried to investigate the melting behavior of incorporated solvents. From the differential scanning calorimetry results of a gel polymer electrolyte prepared with $LiBF_4$–EC/DMC, two endothermic peaks were found at −6.1 and 18.1 °C that were attributable to the melting of DMC and EC, respectively. This indicates that the freezing of solvents in the gel polymer electrolyte occurred on cooling, and so the solvent-rich domains of EC and DMC existed as crystalline solids at a low temperature. However, a gel polymer electrolyte prepared with $LiPF_6$–EC/DMC did not exhibit any endothermic peaks at greater than −30 °C; this suggested that solvents in the gel polymer electrolyte were not frozen even at −30 °C and that the strong interactions that occurred in the polymer–solvent–salt mixture hindered the ordering of solvent molecules. In a comparison of the melting behaviors of the two electrolyte solutions added to the membrane, a pure $LiBF_4$–EC/DMC solution showed two melting peaks at −10.7 and 24.4 °C, and a pure $LiPF_6$–EC/DMC solution showed one melting peak at 31.4 °C. These results suggest that the type of salt has a large influence on the melting behavior of incorporated solvents in both pure liquid electrolytes and gel polymer electrolytes.

The electrochemical stability of the gel polymer electrolytes was evaluated with linear sweep voltammetric measurements. The porous membranes prepared by phase inversion exhibited a cross-sectional asymmetry, as shown in Figure 1. Therefore, it was important to check the decomposition voltages on both surfaces. Figure 3 illustrates linear sweep voltammetry curves of cells prepared with gel polymer electrolytes containing different electrolyte solutions. Solid and dashed lines refer to the measurements performed with an SS working electrode in contact with upper and lower sides of the porous membranes, respectively. It seems that the orientation of the porous membrane in the cell little affected the electrochemical stability of the gel polymer electrolyte. For both systems, the current onsets were detected around 4.4–4.6 V versus Li and could be assigned to the decomposition voltages of the gel polymer electrolytes. This result makes these gel polymer electrolytes acceptable for high-voltage cathodes such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$. The oxidation current for the $LiBF_4$-based gel polymer electrolyte was higher than that of the $LiPF_6$-based gel polymer electrolyte at a high-voltage region; this means that the gel polymer electrolyte prepared via soaking in $LiPF_6$–EC/DMC was more resistant to oxidation.

CONCLUSIONS

Porous membranes based on the AM copolymer were prepared by phase inversion. The physical

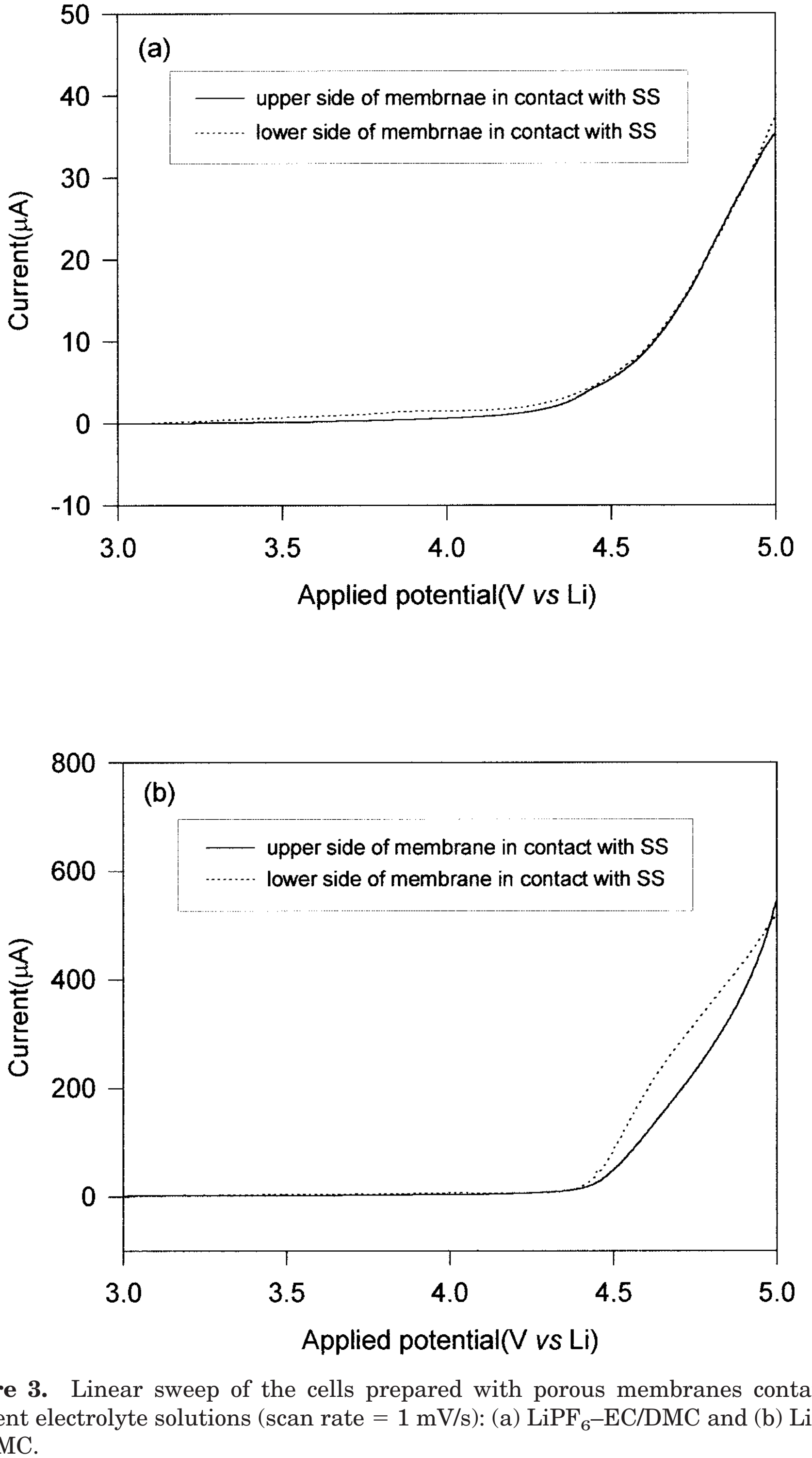


Figure 3. Linear sweep of the cells prepared with porous membranes containing different electrolyte solutions (scan rate = 1 mV/s): (a) $LiPF_6$–EC/DMC and (b) $LiBF_4$–EC/DMC.

properties of the porous membranes, such as pore volume, pore size, and pore structure, could be controlled by changes in the evaporation time before phase inversion. With these porous membranes, gel polymer electrolytes were prepared via soaking in electrolyte solutions. The porosity of the membrane was shown to play an important role in determining the uptake of the electrolyte solution, the ionic conductivity, and the mechanical strength of the gel polymer electrolytes. Gel polymer electrolytes prepared with membranes of 37% porosity were the most desirable for both high ionic conductivity and good mechanical strength. Ionic conductivity reached 6.4 $\times 10^{-4}$ S/cm in the gel polymer electrolyte containing 66% $LiPF_6$–EC/DMC, and the electrolyte solution was well encapsulated in the porous membrane by physical gelation. In terms of subambient-temperature conductivity, the gel polymer electrolyte containing $LiPF_6$–EC/DMC exhibited higher ionic conductivity than that containing $LiBF_4$–EC/DMC. Decomposition voltages exceeding 4.4 V made them suitable for applications in lithium-ion polymer cells. More detailed studies on the performances of lithium-ion polymer cells employing these porous membranes are in progress.

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