

리튬 이차전지 고분자 전해질용 다공성 Poly(vinylidene fluoride)/Poly(ethylene carbonate) 막의 특성 연구

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Characterization of Porous Poly(vinylidene fluoride)/ Poly(ethylene carbonate) Membranes for Polymer Electrolytes of Lithium Secondary Batteries

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1. Introduction

So far the most practical polymer electrolytes are gel systems, which contain a polymeric matrix, a lithium salt, and aprotic organic solvents. This has met with success but has had disadvantages that the addition of solvents promotes deterioration of the electrolyte's mechanical properties and increases its reactivity towards the lithium metal anode.[1] In order to alleviate the problems inevitably caused by the leakage and evaporation of organic solvents in gel polymer electrolytes, we report the novel solvent-free polymer electrolytes with porous poly(vinylidene fluoride-co-hexafluoro propylene) (P(VdF-HFP)) /poly(ethylene oxide-co-ethylene carbonate) (P(EO-EC)) membranes filled with viscous P(EO-EC).

2. Experimental

The P(EO-EC) ($M_n = 1,800$) was synthesized via ring opening polymerization using ethylene carbonate (EC, Aldrich) which is usually used as a liquid electrolyte in gel polymer electrolytes. The porous P(VdF-HFP)/P(EO-EC) blend membranes were prepared by a phase inversion method and some of them were annealed at 110 °C for 2 h in

order to improve mechanical properties. The prepared porous membranes were filled with P(EO-EC)/LiCF₃SO₃ mixture by using vacuum and finally the solvent-free polymer electrolytes were obtained. M-VxEy and E-VxEy here denote the porous Membrane with blend composition of P(VdF-HFP)/P(EO-EC) (x/y by wt%) and the polymer Electrolyte filled with the P(EO-EC)/LiCF₃SO₃ mixture inside pores of the M-VxEy membrane, respectively.

The porosity of these membranes was measured by immersing the porous membranes into *n*-butanol for 1 h and then calculated by the following equation:

$$\text{porosity (\%)} = \frac{m_a/\rho_a}{m_a/\rho_a + m_p/\rho_p} \quad (1)$$

where m_p is the weight of dried membranes, m_a is the weight of *n*-butanol absorbed in the wet membranes, ρ_a is the density of *n*-butanol, and ρ_p is the density of membranes. The microstructure of dried porous membranes was observed using JSM-6330F field-emission scanning electron microscopy (FE-SEM). Mechanical strength of porous membranes was measured with a strain rate of 20 mm min⁻¹ according to the ASTM 882 procedure with a LLOYD LR10K universal testing instrument. Ionic conductivity was measured by the complex impedance technique in the temperature range of 5 to 95 °C and frequency range of 0.1 Hz to 1 MHz using a Zahner Electik IM6 impedance analyzer. The specimens for conductivity measurements were prepared by sandwiching the polymer electrolytes between two 1.7 × 1.7 cm²-sized stainless steel (SS) electrodes. All assemblies of samples were performed in a dry room.

3. Results and Discussion

The porosity of unannealed and annealed membranes increases with increasing P(EO-EC) composition in membranes and these data are listed in Table 1. This shows that the introduction of viscous P(EO-EC) in membranes results in high porosity because the evaporation of non-solvent in flexible membranes is easier than that in rigid membranes. Therefore, high porosity of the membranes can be obtained by adding viscous P(EO-EC) in membranes and their

maximum porosity reaches up to 65% for unannealed M-V6E4.

Table 1. Porosity data of annealed and unannealed membranes

Membranes	Porosity (%)		Membranes	Porosity (%)	
	Annealed	Unannealed		Annealed	Unannealed
M-V10E0	54.2	54.3	M-V7E3	61.6	61.8
M-V9E1	56.8	57.4	M-V6E4	64.2	64.6
M-V8E2	58.9	59.1	M-V5E5	62.4	62.9

Typical SEM micrographs of the surface of selected samples (i.e., M-V6E4 and E-V6E4) are presented in Fig. 1. The porous membranes (Fig. 1a) are the matrix of the solvent-free polymer electrolytes (Fig. 1c) and viscous P(EO-EC) well trapped in the pores of the membranes plays a role of ion conduction. Interestingly, the morphology of the membrane annealed at 110 °C for 2 h (Fig. 1b) shows highly ordered and cross-linked pore structure, i.e., honeycomb-like structure, indicating that their mechanical properties may be remarkably improved.

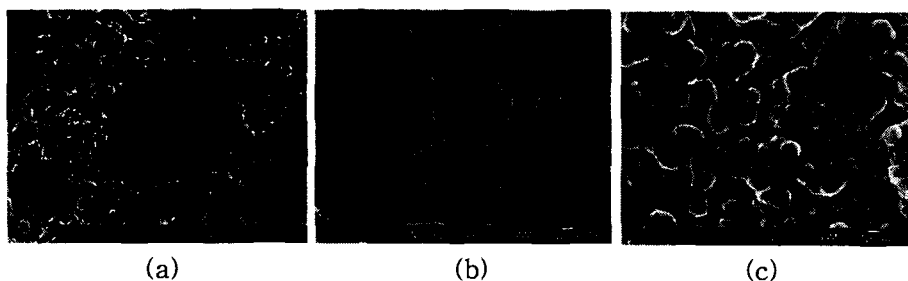


Figure 1. Typical SEM micrographs of porous membranes and polymer electrolytes: unannealed M-V6E4 (a); annealed M-V6E4 (b); E-V6E4 filled with viscous P(EO-EC) (c).

In addition, the pore size of porous membranes is somewhat reduced by annealing process. It was reported that the pore size of membranes could be reduced by changing casting conditions, polymer solution compositions, coagulation bath compositions, and annealing.[2] From these results, it is estimated that the relative composition of P(EO-EC) in membranes is proved to play a critical role in determining the

morphology and the porosity of the porous membrane.

In the case of unannealed membranes, tensile strength gradually decreases with increasing P(EO-EC) composition in membranes, while elongation gradually increases up to 30 wt% of P(EO-EC) composition in membranes. However, in the case of annealed membranes, tensile strength and Young's modulus significantly increase. These results clearly demonstrate that the mechanical strength of porous membranes can be enhanced by annealing technique while keeping the P(EO-EC) content high.

All polymer electrolytes with the optimized lithium-salt concentration (1.5 mmol LiTf/g-P(EO-EC)) obey Arrhenius relationship, showing a linear enhancement of the ionic conductivity with increasing the temperature. The room temperature ionic conductivity of the electrolytes reaches a maximum value of $3.7 \times 10^{-5} \text{ S cm}^{-1}$ for E-V6E4 prepared using unannealed M-V6E4, which is in good accordance with the trend of the highest porosity of the membranes. On the other hand, the electrochemical stability window is at least 5 V for polymer electrolytes. This high stability is probably due to the absence of any liquids.[1]

Therefore, overall results indicate that novel solvent-free polymer electrolytes based on porous P(VdF-HFP)/P(EO-EC) membranes filled with viscous P(EO-EC) can be useful as a new candidate for lithium secondary batteries because they show marked electrochemical performance.

5. References

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