

**Characterization of Novel Polymer Electrolytes for
Lithium-ion Secondary Batteries I:
P(VdF-HFP)/ P(EO-EC) Blend Membranes with
Pores Immersed by P(EO-EC)**

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Organic solvent such as ethylene carbonate (EC) or propylene carbonate (PC) is usually added to form gel-type polymer electrolyte for Li-ion secondary battery. Despite its high ionic conductivity ($\sim 10^{-3}$ S/cm) compared to the solid-type polymer electrolyte, the gel polymer electrolyte has critical drawbacks ascribed to the leakage and evaporation of the solvent, thereby resulting in gradual deterioration of its overall electrochemical performance over prolonged period.

The purpose of this study is to overcome the problems inevitably caused by the solvent leakage and evaporation without sacrificing the ionic conductivity of gel-type electrolytes. In order to accomplish the objective, the porous poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-HFP)]/poly(ethylene oxide-co-ethylene carbonate) [P(EO-EC)] blend membranes were first prepared by a phase-inversion method, in which the porosity of the membrane could reach up to $\sim 65\%$ depending on P(EO-EC) composition of the blend. Then, the viscous P(EO-EC), playing a role of ion conduction, was immersed and filled into the pores of the membranes instead of the conventional solvent, EC or PC. Thus, a novel solvent-free electrolytes consisted of the porous P(VdF-HFP)/P(EO-EC) membrane with pores immersed by P(EO-EC) were produced. The solvent-free electrolytes were subjected to A.C. impedance analysis at temperature ranging from 5 to 95 °C and their temperature dependence of ionic conductivity was shown to obey Arrhenius relationship, implying there was no abrupt decrease of ion conductivity even at lower

temperatures. The ionic conductivity, σ of the electrolytes at room temperature reached a maximum value of $\sim 4 \times 10^{-5}$ S/cm for the P(VdF-HFP)/P(EO-EC) membrane prepared by the blend composition of 60/40, which was in good accordance with the trend of porosity of the membranes depending on P(EO-EC) composition in the blend (Fig. 1). The electrochemical stability of the electrolytes tested by cyclic voltammetry showed that the cathodic stability did not indicate any electrochemical oxidation until the potential reached 6.0 V. This remarkable electrochemical stability can shed light on the possible practical application in high-voltage Li-ion polymer batteries.

Overall, it is concluded that immersion of polymeric material into the porous membrane is a new attempt to prepare polymer electrolytes for Li-ion secondary batteries and the resulting P(VdF-HFP)/P(EO-EC) electrolyte with pores filled with P(EO-EC) provided an another promising candidate for practical solvent-free electrolytes.

References

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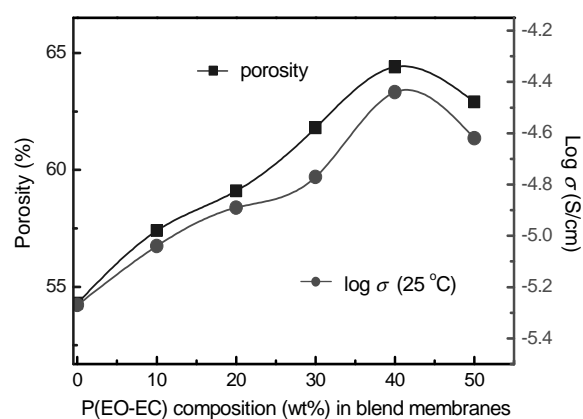


Figure 1. Relationship between porosity and room-temperature ionic conductivity for solvent-free P(VdF-HFP)/P(EO-EC) electrolytes.