Effect of Solvent on the Properties of Nanoparticle-Filled Polymer Electrolytes Prepared by Phase Inversion Technique

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Porous polymer electrolytes using poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) as a host polymer have been studied for the application to lithium rechargeable battery systems. Inorganic fillers such as fumed silica $(SiO_2)^1$ and titania $(TiO_2)^{2,3}$ have adopted to the electrolyte system in order to enhance the mechanical strength as well as electrochemical properties. However, these systems, prepared by conventional casting method, easily yield somewhat compact structure, compared to those by phase inversion techniques. Phase inversion technique may be a good method to obtain highly porous structure developed within the membrane. The porous structure can be formed during the mutual diffusion processes between solvent and non-solvent species. As a next topic followed by the previous study,⁴ we investigate the physical and electrochemical properties of nanoparticle (SiO_2, TiO_2) -filled PVdF-HFP polymer electrolytes prepared by phase inversion techniques using different two solvents and water.

We used KynarFlex 2801 (HFP content of 12 mol%, Atofina Chemicals) as PVdF-HFP, Cab-O-Sil TS-530 (Cabot) as fumed silica (SiO₂) and PC-101 (Japan Titan) as anatase TiO₂ fillers. We also used two kinds of solvent, such as N-methyl-2-pyrrolidone (NMP, Aldrich) and dimethylacetamide (DMA, Aldrich). Electrolyte solution used was 1M LiPF₆ dissolved in ethylene carbonate/ dimethyl carbonate (1:1 w/w). Viscous slurries were obtained by dissolving polymer and different amount of filler in solvent. The slurry was spread on a clean glass plate by doctor blade apparatus. Phase inversion membranes were obtained by dipping immediately the coated glass plate into the flowing water, and then dried in an ambient condition for 24 h. First, we determined the filler content range in which self-standing film can be obtained. Characterization of polymer electrolyte membranes was performed by DSC (thermal property), XRD (crystallinity), SEM (morphology), uptake of electrolyte solution, and some electrochemical properties including ionic conductivity, electrochemical stability, interfacial resistance, and so on.

During the preparation of phase inversion film, different solvents are found to produce different porous structure due to different relative diffusion rate against that of nonsolvent molecules. As shown in Figs.1 and 2, the film using NMP has more closely packed pore structure than that using DMA. In this comparison, there is some mismatch in filler content, but the general trend between the films is proved as same. Precise comparison based on physical and electrochemical properties (including the ionic conductivity in Fig.3) will be discussed in the presentation.



Fig.1 Cross-sectional image of PVdF-HFP/TiO₂ (5 wt%) film prepared by phase inversion using the solvent NMP



Fig.2 Cross-sectional image of PVdF-HFP/TiO₂(30 wt%) film prepared by phase inversion using the solvent DMA



Fig.3. Arrhenius plot of phase inversion PVdF-HFP/TiO₂ electrolytes prepared by using different solvents of NMP and DMA.

References

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