Preparation and Characterization of Asymmetric Composite Polymer Electrolytes for Lithium Metal Polymer Batteries

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An asymmetric composite polymer electrolyte composed of porous polymer matrix which micro-porous layer based on the polyethylene acts as a support and submicro-porous layer is introduced on one side of the micro-porous layer through a coating process and ethylene carbonate/dimethyl carbonate/LiPF$_6$ liquid solution occupying the pores has been prepared. The maximum ionic conductivity of this system was 7.0×10^{-3} S/cm at the ambient temperature. The conductivity seems to be significantly affected by the uptake amount of liquid electrolyte within the matrix.

Introduction

Worldwide research and developmental efforts are currently underway to fabricate lithium metal polymer batteries(LMPB) using lithium(Li) metal as anode and polymer electrolyte as its electrolyte, respectively[1,2]. Potential fields of application for LMPB range from small portable electronic device and personal communication equipment such as IMT-2000 or next generation PDA to electric vehicles(EV) due to a potential advantage of high energy density.

However, since Li metal is very corrosive and highly reactive toward electrolytes and impurities such as residual solvents, humid air, and even in oxygen atmosphere, a non-uniform and thick passive layer is easily formed on the electrode surface[3-7]. In addition, since the charge/discharge reactions of Li metal correspond to the electrochemical deposition/dissolution of Li$^+$, undesirable morphologies of Li anode such as dendrite and dead Li can be seriously formed on the Li anode surface[8-12]. Among them, the dendrite formation and growth crucially affect on the safety and cycle performance of LMPB.

In this study, we have introduced a novel polymer electrolyte for LMPB, an asymmetric composite polymer electrolyte having combination of micro-porous and submicro-porous layer physically, incompatible and compatible layer with liquid electrolytes chemically. Micro-porous and incompatible layer acts as a support and main ion conduction medium. Submicro-porous and compatible layer is introduced on one side of micro-porous layer, which shows good accommodation of a liquid electrolyte. The submicro-porous layer would be contacted with Li anode surface to effectively control the dendrite growth and protect Li anode from corrosion and side reaction. The ionic conductivities of the porous matrix with coated thickness of the submicro-porous layer and various uptake amounts have been investigated.

Experimental

Preparation of Asymmetric Composite Membranes

The appropriate amount of P(VdF-co-HFP) and silanized fumed silica to control the compatibility between P(VdF-co-HFP) and liquid electrolytes were completely dissolved in acetone in a polyethylene(PE) bottle at 50 °C for 1 h. After complete dissolution, the solution was homogenized for 24 h at room temperature in a laboratory ball mill. The viscous solution was coated on one side of micro-porous membrane(PE, Asahi Kasei, porosity 40 %) with a doctor blade. The coated membrane was then vacuum dried at 40 °C for 24 h. The schematic feature of the prepared asymmetric composite membrane is shown in Figure 1.
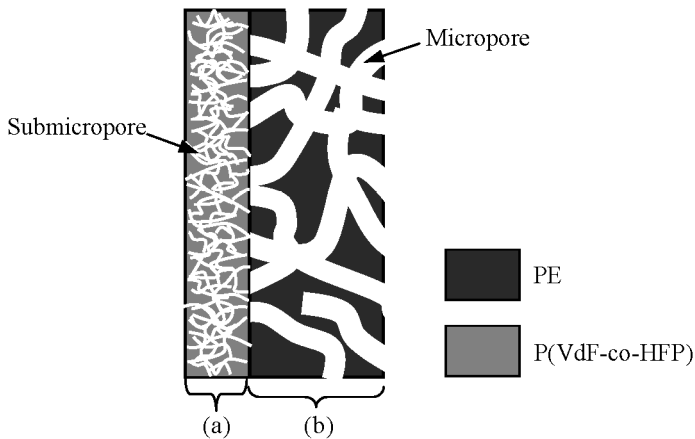

Figure 1. The Schematic feature of the prepared asymmetric composite membrane system: (a) submicro-porous and compatible layer based on P(VdF-co-HFP) (b) micro-porous and incompatible layer based on PE.

Scanning Electron Microscopic (SEM) Measurements

The morphologies of the asymmetric composite membranes were investigated by using a scanning electron microscope(Philips SEM 535M). Specimens for the SEM image of the fractured side were prepared in liquid nitrogen.

Uptake of Liquid Electrolytes Measurements

The porous films were immersed in a liquid electrolyte solution for a proper time. The uptake amount of liquid electrolyte into porous matrix film was measured and calculated as follows:

$$\text{Uptake amount (wt\%)} = [(W_a - W_b) / W_b] \times 100 \qquad (1)$$

where W_b and W_a represent the weight of the samples before and after immersion in the liquid

electrolyte solution, respectively. Prior to measurement, the wetted films were lightly patted with a tissue to remove the liquid electrolyte on the film surface. All these experiments were carried out in a glove box under argon atmosphere with less than 0.5 ppm water.

A.C. Impedance Spectroscopic Measurements

The specimen for ionic conductivity measurement was prepared by sandwiching the polymer electrolyte between two stainless steel electrodes of which the size was 2 cm × 2 cm. The sandwich was vacuum-sealed in an aluminized PE bag in order to avoid its contamination by humidity. All these experiments were also carried out in a glove box under argon atmosphere. Impedance of the specimen was measured over the frequency range of 100 Hz ~ 10 MHz using the Solartron 1255 frequency response analyzer(FRA). The data were transmitted from the FRA to a personal computer through the GPIB interface.

Results and discussion

Cross-Sectional Structure of Polymer Matrix with Coating Solution Concentration

We have prepared various asymmetric composite membranes with the coating concentration of P(VdF-co-HFP)/silanized fumed silica/acetone solution from 2 to 17 wt%. In order to measure the coated thickness of the films, the detailed cross-sectional regions were investigated by SEM.
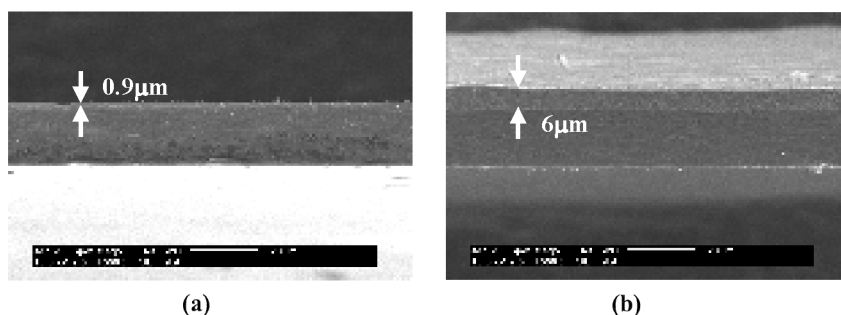

| (a) | (b) |

Figure 2. Typical cross-sectional SEM images(× 1,000) of the asymmetric composite membranes as a function of coating solution concentration: (a) 2 wt% (b) 5 wt%.

Figure 2 reveals the typical SEM images of cross-sections of asymmetric composite membranes prepared. The upper one is the submicro-porous and compatible layer and the lower one is the micro-porous and incompatible layer based on PE membrane where the film thickness is 25 μm. It is observed that the thickness of upper layer increases as the coating solution concentration increases. As shown in Figure 2 (a) and (b), the thickness of submicro-porous was 0.9 and 6 μm when the solution concentration was 2 and 5wt%, respectively. The measured thickness of the submicro-porous layers in asymmetric composite membranes is given in Table 1.

Table 1. Measured thickness of the submicro-porous layers in asymmetric composite membranes by SEM.

Sol'n conc.(wt%)	2	5	10	15	17
Thickness(μm)	0.9	6	11	18	20

Uptake of Liquid Electrolytes into Porous Matrix with Coated Thickness

Figure 3 shows the uptake amount of the liquid electrolytes(1M LiPF$_6$ in EC/DMC(1/1, w/w)) into the asymmetric composite membranes as a function of soaking time and the coated thickness. For comparison, the bare micro-porous PE membrane was also soaked in the same electrolyte solution(0 μm case). For all cases, it could be explained that the initial increase of uptake might be a result of selective filling of micro and submicro-pores within the matrix by liquid electrolyte through the capillary phenomena. Further and continuous increase of uptake with soaking time seems that the membranes are swollen by absorbing the electrolytes through free volumes between the polymer chains or fibrils within non-porous matrix[13,14].
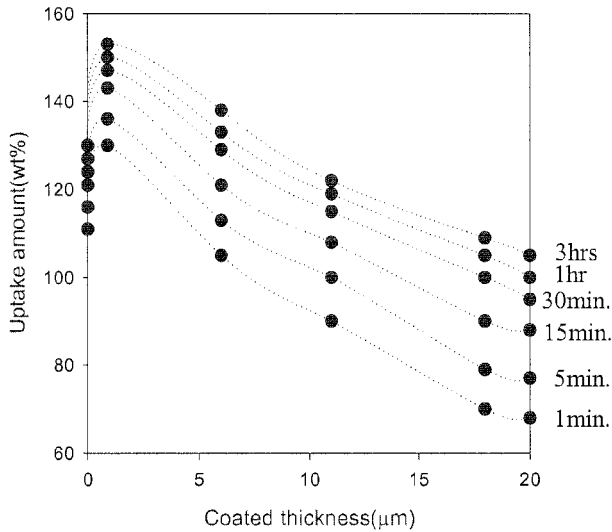

Figure 3. Uptake amount of liquid electrolyte into porous membrane as a function of coated thickness at different soaking time.

For 0.9 μm coated case, it shows the highest uptake amount over the soaking time. It could be understood that the low wettability problem of bare PE membrane as a non-polar polymer was improved by slightly coating of the P(VdF-co-HFP)/silanized fumed silica composite, which shows compatibility with the liquid electrolytes due to the interaction between the fluorine group within the polymer chain or silica and organic solvent in the

liquid electrolytes[15-17]. However, the uptake behavior is found to linearly decrease as the coated thickness increases. The linear decrease of liquid electrolyte uptake seems to be caused by stopping up the pores of PE membrane surface and the inhibition of penetration of electrolytes through the too thick submicro-porous layer into micro-porous matrix in PE membrane with the coated thickness.

Ionic Conductivities of Polymer Electrolytes with Coated Thickness

Figure 4 shows the ionic conductivities of the asymmetric composite polymer electrolytes as a function of coated thickness of submicro-porous layer at various soaking time. The maximum ionic conductivity of the polymer electrolytes was 7.0×10^{-3} S/cm at the ambient temperature when the coated thickness was 0.9 µm and the soaking time was 3 hrs. Then, it decrease as the coated thickness increases.
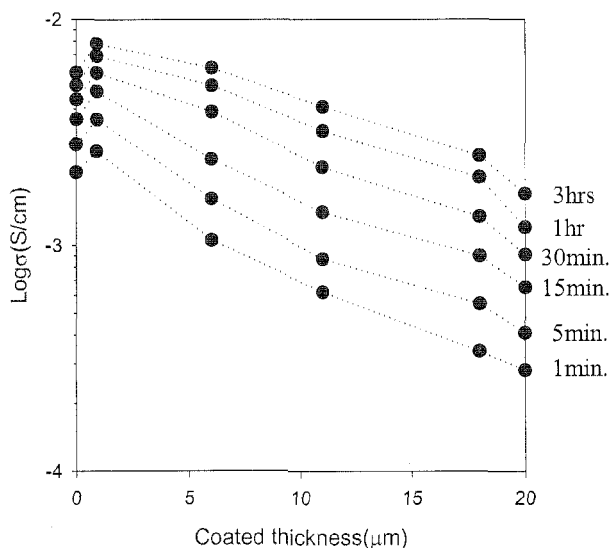

Figure 4. Ionic conductivities of the polymer electrolytes as a function of coated thickness at different soaking time(liquid electrolyte: 1M $LiPF_6$ in EC/DMC (1/1, w/w) mixture, $2 \times 2cm^2$)

When the polymer electrolytes have the highest uptake amount as shown in Figure 3, the highest ionic conductivity was obtained. Since the ionic conductivity behavior of the polymer electrolytes with the coated thickness is very similar with that of uptake amount, the conductivity seems to be significantly affected by the uptake amount of liquid electrolyte within the matrix. The decrease in the absorbed amount of the liquid electrolytes into the porous matrix would make the number of charge carrier decrease and ion conduction path more tortuous[18,19]. On the other hand, ions in the liquid electrolytes flow promptly toward the electrode through each conduction channel when the channels are fully developed and the conduction path is connected well from the one electrode to the opposite one like 0.9µm coated case as the liquid electrolyte uptake increases.

Conclusions

The novel polymer electrolytes based on the asymmetric composite membrane composed of micro-porous and submicro-porous layer has been prepared. The maximum ionic conductivity was 7.0×10^{-3} S/cm at the ambient temperature when the coated thickness was 0.9 μm and the soaking time was 3 hrs. The conductivity seems to be strongly correlated with the amount of the liquid electrolyte uptake within the matrix.

Acknowledgements

References

1. J.R. MacCallum and C.A. Vincent (1987) Polymer Electrolyte Reviews, vol. 1, Elsevier Applied Science, U.K.
2. M. Alamgir, K.M. Abraham, in: G. Pistoia (Ed.) (1994) Lithium Batteries, vol. 1, Elsevier Applied Science, U.K.
3. E. Peled (1979) J. Electrochem. Soc., 126:2047
4. D. Fauteux (1985) Solid State Ionics, 17:133
5. M. Hiratani, K. Miyauchi, and T. Kudo (1998) Solid State Ionics, 28-30:1431
6. M.Z.A. Munshi, R. Gopaliengar, and B.B. Owens (1988) Solid State Ionics, 27:259
7. M. Arakawa, S. Tobishima, Y. Nemoto, and M. Ichimura (1993) J. Power Sources, 43-44:27
8. V.R. Koch (1979) J. Electrochem. Soc., 126:181
9. K. Kanamura, S. Shiraishi, H. Tamura, and Z. Takehara (1994) J. Electrochem. Soc., 141:2379
10. D. Aurbach, B. Markovsky, A. Shechter, and Y. Ein-Eli (1996) J. Electrochem. Soc., 143:3809
11. D. Peramunage, D.M. Pasquariello, and K.M. Abraham (1995) J. Electrochem. Soc., 142:1789
12. B. Scrosati, G.B. Appetecchi, and F. Croce (1995) Electrochimi. Acta, 40:991
13. J.M. Tarascon, A.S. Gozdz, C. Schmutz, F. Shokoohi, and P.C. Warren (1996) Solid State Ionics, 86-88:49
14. D.W. Kim, K.A. Noh, H.S. Min, D.W. Kang, and Y.K. Sun (2002) Electrochem. & Solid-State Lett., 5:A63
15. S.L. Paik and G. Terzaghi (1995) J. Power Sources, 53:283
16. C.H. Kim, H.T. Kim, S.I. Moon, M.S. Yoon, and J.K. Park (1996) J. Polym. Sci., Polym. Phys., 34:2709
17. K.M. Kim, K.S. Ryu, S.G. Kang, S.H. Chang, and I.J. Chung (2001) Macromol. Chem. Phys., 202:866
18. Y.G. Lee and J.K. Park (2001) J. Power Sources, 97-98:616
19. C.H. Kim, H.T. Kim, and J.K. Park (1996) J. Appl. Polym. Sci., 60:1773