Polymer Bulletin 49, 63-68 (2002)

Polymer Bulletin

Effect of silica on the interfacial stability of the PEO-based polymer electrolytes

Baik-Hyun Lee, Nam-Soon Choi, Jung-Ki Park

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea
e-mail: leebh@cais.kaust.ac.kr

Received: 7 May 2002/ Revised version: 10 July 2002/ Accepted: 12 July 2002

Summary

In order to evaluate the effect of silica on stabilizing the interface of lithium metal electrode/solid polymer electrolyte, the cyclic behavior for silica-free and silica-containing polymer electrolyte under electrical stress was investigated using cyclic voltammetry. These electrolytes have an ionic conductivity of the order 10^{-4} S/cm at above 60°C and most importantly the introduction of hydrophilic silica in PEO-based polymer electrolyte has brought about the enhanced stability of lithium metal electrode/polymer electrolyte interface especially under electrical stress. This in turn supports the suitability of the composite polymer electrolytes with hydrophilic silica for fabrication of enhanced rechargeable solid lithium polymer batteries.

Introduction

In order to achieve an improvement of energy density and to enable a true solid state configuration for enhanced versatility in battery design and reduced manufacturing costs, the replacement of liquid lithium-ion battery with a lithium polymer battery(LPB) which uses lithium metal as electrode is very important in the lithium battery technology. For polymer electrolytes of LPB, poly(ethylene oxide), PEO, has been extensively studied due to high ionic conductivity in the amorphous phase, high capacity in salt complexation, mechanical flexibility, and corrosion resistance. This material has lower values of ionic conductivity (less than 10^{-6} S/cm) at room temperature, and it seems that PEO-based LPB has a suitability for electric vehicles operating at relatively high temperature(70~90°C). To enhance the ionic conductivity of polymer electrolytes, recently composite polymer electrolytes have been prepared for PEO-based polymer electrolytes with inorganic particle such as SiO_2, Al_2O_3, TiO_2, and γ-$LiAlO_2$, and their increased ion conductivities have often been reported[1-9]. B. Scrosati *et al.*[3] showed that the addition of nanometric fillers (SiO_2, TiO_2) to $P(EO)_nLiClO_4$ polymer electrolytes induces an improvement in the transport properties and that the increase in conductivity and transference number was attributed to the enhancement of the degree of the amorphous phase in the polymer matrix.

What is more important is the optimization and control of the lithium electrode/polymer electrolyte interface. It is now well established that the growth of the lithium passivation layer is increased by the presence of liquid components and/or impurities in the polymer electrolyte. By solvent-free hot-pressing technique, G.B. Appetecchi *et al.*[2] made composite polymer electrolytes with an exceptionally high stability with the lithium metal electrode in the polymer electrolyte of PEO-$LiBF_4$-γ-$LiAlO_2$. They proposed that a main reason of having a stable interfacial property during storage is the trapping of residual impurities by introduction of inorganic particles. It is expected, however, that the introduction of inorganic filler produces other contribution to interfacial stability by anchoring the salt anions or polymer molecules in addition to trapping the impurities especially under electrical stress. In order to confirm these reasonings, we tried to evaluate the interfacial stability of composite polymer electrolyte by using nanosized silica particles with different surface properties, that is, hydrophilic and hydrophobic properties. For this, the cyclic behavior of PEO-based composite polymer electrolyte modified with nanosized silica was systematically analyzed.

Experimental

Preparation of polymer electrolytes

The polymer electrolyte films were prepared by the solvent casting technique using PEO(Aldrich, M.W. = 6×10^5 g/mol), $LiClO_4$(Aldrich), and nanosized silica(EH5: hydrophilic, TS-530:hydrophobic, Cab-o-sil). The [EO]:[Li] ratio of the polymer complex was 16:1. Silica and lithium salt were dried for 24 h at 130°C under vacuum. First, silica and lithium salt were dissolved in acetonitrile, and the solution was sonicated. After sonication, PEO was added and completely dissolved, resulting in a homogenized colloidal solution which was cast into a film of about 200°C thickness.

DSC measurements

Glass transition temperatures (T_g) and melting temperature(T_m) of the polymer electrolytes were measured by using a differential scanning calorimeter (DuPont TA 2000 DSC). Each sample was scanned at a heating rate of 10°C/min within an appropriate temperature range under nitrogen atmosphere.

Electrical measurements

The ionic conductivities and interfacial resistances of the polymer electrolytes were obtained by a.c. complex impedance analysis using a Solatron 1255 frequency response analyzer (FRA) over a frequency range of 10Hz~1MHz. The cyclic voltammetry(CV) experiments were carried out on a lithium working electrode with lithium electrode as the counter and reference electrode in the potential range of –3.0 to 3.0V vs Li at a scanning rate of 10mV/sec using a Solatron 1287 electrochemical interface analyzer. Before the cyclic voltammetry experiments, the cells were equilibrated at 65°C for 1 day in order to stabilize the interface between the polymer electrolyte and the lithium electrode.

Results and discussion

Thermal properties and Conductivity of PEO-based polymer electrolytes

The results of the DSC and conductivity measurements of $(PEO)_{16}LiClO_4$ and $(PEO)_{16}LiClO_4$ -SiO_2 polymer electrolyte are summarised in Table 1. With the addition of SiO_2 particles, there was a little decrease in the crystallinity of PEO. The decrease in the PEO crystallinity was a little more significant in the polymer electrolyte containing hydrophilic silica(EH5) than that containing hydrophobic silica(TS530). It seems that the silanol(Si-OH) group of the surface of the hydrophilic silica interacts with the ether group of PEO to disrupt the crystalline structure of PEO phase. Useful conductivity(that is, above 10^{-4} S/cm) was obtained at temperatures higher than 60°C, and so we tested the stability of the lithium electrode/polymer electrolyte interface at 65°C

Table. 1 DSC & conductivity measurements

Samples	T_g(°C)	T_m(°C)	Δ H(J/g)	Conductivity(S/cm), 65°C
PEO_{16}:$LiClO_4$	-13.0	45.8	82.4	2.64×10^{-4}
PEO_{16}:$LiClO_4$ +Silica(EH5) 10 wt%[a]	-12.4	44.8	69.0	1.96×10^{-4}
PEO_{16}:$LiClO_4$ +Silica(TS530) 10 wt%[a]	-12.6	46.3	72.8	2.15×10^{-4}

[a] The % amount of silica added is based on the weight of PEO and salt

Effect of silica on interfacial stability of polymer electrolytes during storage

The interfacial resistance and stability for the lithium/PEO-based polymer electrolyte during storage were studied by impedance spectroscopy. A plot of the interfacial resistance of the polymer electrolytes against lithium electrodes is given in Fig.1. The silica-free PEO-based polymer electrolyte is not shown to form a stable interface with lithium as indicated by the continuous increase in interfacial resistance with time.

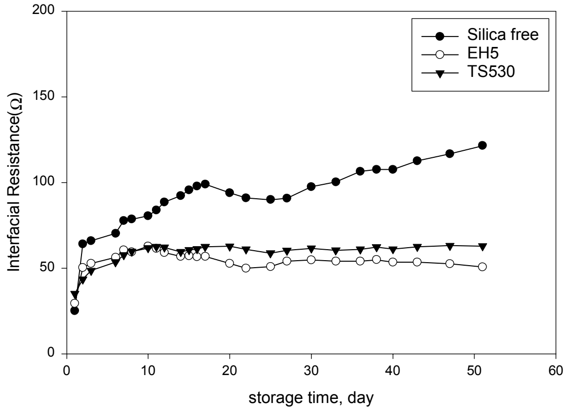

Fig. 1. Time evolution of the interfacial resistance of the PEO-based polymer electrolytes without/with silica at 65°C.

However the PEO-based polymer electrolyte with silica exhibited more stable interface with the Li electrode. This different interfacial response between the silica-free polymer electrolyte and the silica-containing polymer electrolyte during storage is expected to result from the trapping behavior of impurities or solvent molecules by silica, and it is consistent with the previous results of G. B. Appetecchi, et al[2].

Effect of silica on interfacial stability of polymer electrolytes under electrical stress

In order to investigate the interfacial stability of the PEO-based composite polymer electrolytes with lithium electrode under cyclic electrical stress, the impedance of lithium symmetric cell was monitored as a function of lithium plating and stripping in the potential range between –3.0V and 3.0V at 65°C. The stability of the interface between the lithium metal electrode and the polymer electrolytes has been evaluated by monitoring the impedance response of lithium symmetric cells kept under open-circuit conditions. Fig. 2 shows the change of interfacial resistance with cycles for the lithium symmetric cells based on different polymer electrolytes. It is found that the interfacial resistances of the silica-free and the hydrophobic silica-containing polymer electrolyte increase significantly by repeating cycles compared to that of polymer electrolyte with hydrophilic silica. This result is not consistent with the one from storage experiment for hydrophobic silica-containing polymer electrolyte. It seems that there is a significant growth of passivation layer for the silica-free and the hydrophobic silica-containing polymer electrolyte compared to the polymer electrolyte containing hydrophilic silica during electrical stress. Under electrical stress, the decomposition of anions or polymer molecules may become serious resulting in the growth of passivation layer. ClO_4^- anion can form radicals by decomposition[10], and bring about the degradation of polymer molecule to produce passivating materials at interface. In silica-free and hydrophobic silica-containing polymer electrolyte, ClO_4^- anions may not be efficiently captured in the media during the charge transport. However, in hydrophilic silica-containing polymer electrolyte,

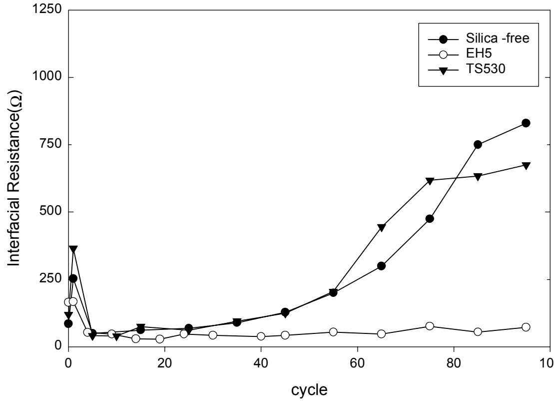

Fig. 2. Scan-number dependence of the interfacial resistance between lithium electrode and polymer electrolyte for the Li/PEO-based polymer electrolyte/Li symmetric cell at 65°C from the results of the impedance spectra.

silica can easily capture the ClO_4^- anions by the interaction of the silanol group of silica with anions. This may be supported by the reported values of transference numbers of PEO-based polymer electrolytes with and without containing silica[7]. It is thus concluded that the introduction of hydrophilic silica into the PEO-based polymer electrolyte retard the excessive formation of passivation layer, and stabilize the interface between polymer electrolyte and lithium electrode.

Fig. 3 illustrates the typical cyclic voltammograms of the Li/PEO-based polymer electrolyte with or without silica/Li cell up to 95 cycles. Fig. 4 represents plots of cycle vs. peak current for the lithium symmetric cells based on the different polymer electrolytes. The peak current behavior of the silica-free and the hydrophobic silica-containing polymer shows a poor reversibility at the initial stage of cycles, and the peak currents greatly decreased from 4~5 mA/cm^2 to about 1mA/cm^2, while the hydrophilic silica-containing polymer electrolyte has a good reversibility and a less reduction in the peak current with cycles. Fig. 5 shows the change of voltage at peak

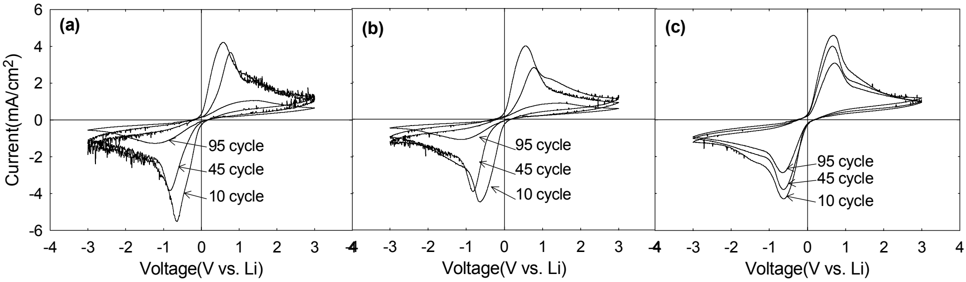

Fig. 3. Cyclic voltammogram of the Li/PEO-based polymer electrolyte/Li symmetric cell at 65°C. (a) Silica-free (b) with hydrophobic silica(TS530) (c) with hydrophilic silica(EH5).

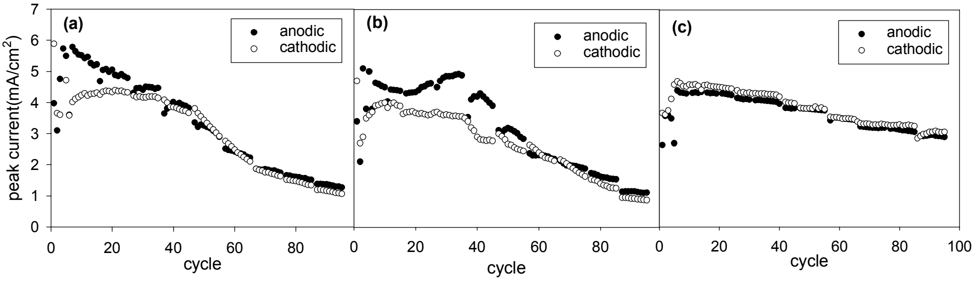

Fig. 4. Scan-number dependence of the plating-stripping peak current of the Li/PEO-based polymer electrolyte/Li symmetric cell at 65°C from the results of cyclic voltammogram. (a) Silica-free (b) with hydrophobic silica(TS530) (c) with hydrophilic silica(EH5).

current as a function of cycle. While in the case of composite polymer electrolyte with hydrophilic silica the voltage at peak current maintains almost the same value of 0.65V, the silica-free and the hydrophobic silica-containing polymer electrolyte show a significant increase of voltage value at peak current, from 0.6V to 1.35V with cycles. From these results, it is clear that the hydrophilic silica-containing polymer electrolyte forms more stable interface.

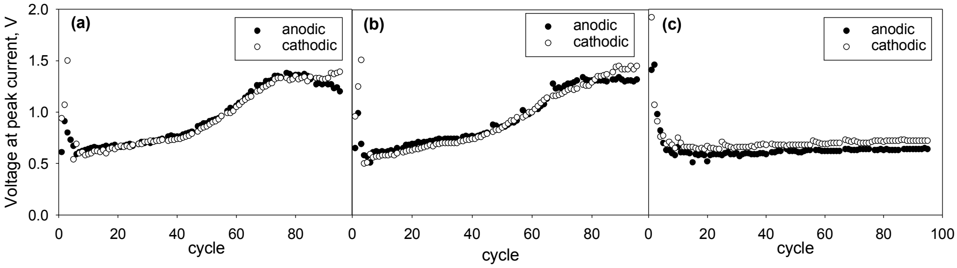

Fig. 5. Scan-number dependence of voltage at the plating-stripping peak current of the Li/PEO -based polymer electrolyte/Li symmetric cell at 65°C from the results of cyclic voltammogram. (a) Silica-free (b) with hydrophobic silica(TS530) (c) with hydrophilic silica(EH5).

References

1. Croce F, Appetecchi GB, Persi L, Scrosati B (1998) Nature 394:456
2. Appetecchi GB, Croce F, Dautzenberg G, Mastragostino M, Ronsi F, Soavi F, Zanelli A, Alessandrini F, Prosini PP (1998) J Electrochem Soc 145:4126
3. Scrosati B, Croce F, Persi L (2000) J Electrochem Soc 147:1718
4. Borghini MC, Mastragostino M, Zanelli A (1997) J Power Sources 68:52
5. Krawiec W, Scanlon LG, Fellner Jr-JP, Vaia RA, Vasudevan S, Giannelis EP (1995) J Power Sources 54:310
6. Tambelli CC, Bloise AC, Rosario AV, Pereira EC, Magon CJ, Donoso JP (2002) Electrochim Acta 47:1677
7. Chung SH, Wang Y, Persi L, Croce F, Greenbaum SG, Scrosati B, Flichta E (2001) J Power Sources 97-98:644
8. Qian X, Gu N, Cheng Z, Yang X, Wang E, Dong S (2001) Electrochim Acta 46:1829
9. Appetecchi GB, Croce F, Persi L, Ronci F, Scrosati B (2000) Electrochim Acta 45:1481
10. MacCaluum JR, Vincent CA (1987) Polymer Electrolyte Reviews-1:Ch.10. Elsevier, London