Polarization behavior of lithium electrode in polymeric solid electrolytes

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Abstract

Complexes of novel polymer matrices and lithium salts have been prepared as polymeric solid electrolytes for lithium batteries. Poly(ethylene oxide)–grafted poly(methylmethacrylate) (PEO–PMMA) and poly(methylsiloxane) (PMS) were used as the matrices. The conductance behavior of the complexes and the basic polarization characteristics of the lithium electrode in the polymeric electrolytes were studied. As high conductivities as 10^{-3} S cm^{-1} were obtained at room temperature for the PMMA-based electrolytes containing some liquid plasticizer. Limiting current densities of 3 to 5 mA cm^{-2} were observed for the anodic and cathodic polarization of the lithium electrode. The transport number of Li$^+$ was approximately unity in 'single-ion type' PMS-based electrolyte, in which the polarization curve of the lithium electrode showed no current hysteresis.

Introduction

Some prototype rechargeable lithium (Li) batteries using so-called polymeric solid electrolytes such as poly(ethylene oxide) (PEO)-based polymer complexes with Li salts have been fabricated [1–4]. This type of battery can be ultra-thin and have high energy density. The major problems of the batteries with polymeric solid electrolytes are relatively low conductivity of the electrolyte at ambient temperature and poor electrical contact at the electrode/electrolyte interface. Therefore, much attention has been directed to the development of new polymer/electrolyte salt systems with better electrical and electrochemical properties. Also the interface behavior of the Li electrode/polymeric electrolyte system has become of interest to many researchers.

We have proposed novel polymer matrices based on poly(methylmethacrylate) (PMMA) and poly(methylsiloxane) (PMS) backbones containing oligo(ethylene oxide) units in their side chains for solid electrolytes of Li batteries [5–7]. In the present work, we studied the conductance behavior of PMMA-based and PMS-based polymeric electrolytes and attempted to improve the conductivity and the Li$^+$ transport number. The basic polarization behavior of the Li negative electrode was measured in the polymeric solid electrolytes and was discussed in connection with the ionic behavior of the electrolyte.
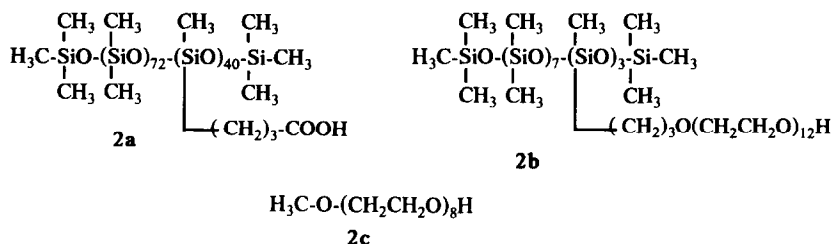
Experimental

Two types of the polymer matrix, PMMA-based and PMS-based polymers, were used in this work. The PMMA-based polymer was synthesized by photo-induced radical

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$$CH_3$$
$$CH_2=CCO_2(CH_2CH_2O)_9CH_3$$
1a

$$CH_3 \qquad CH_3$$
$$CH_2=CCO_2(CH_2CH_2O)_9COC=CH_2$$
1b

Scheme 1. Monomers for PMMA-based electrolytes.

$$CH_3\ CH_3 \quad CH_3\ CH_3$$
$$H_3C-SiO-(SiO)_{72}-(SiO)_{40}-Si-CH_3$$
$$CH_3\ CH_3 \qquad CH_3$$
$$\qquad\qquad\qquad (CH_2)_3-COOH$$
2a

$$CH_3\ CH_3 \quad CH_3\ CH_3$$
$$H_3C-SiO-(SiO)_7-(SiO)_3-Si-CH_3$$
$$CH_3\ CH_3 \qquad CH_3$$
$$\qquad\qquad\qquad (CH_2)_3O(CH_2CH_2O)_{12}H$$
2b

$$H_3C-O-(CH_2CH_2O)_8H$$
2c

Scheme 2. Prepolymers for PMS-based electrolytes.

polymerization of 3:1 (by molar ratio) mixed monomers, methoxypoly(ethylene glycol) monomethacrylate (PEM: 1a) and poly(ethylene glycol) dimethacrylate (PED: 1b) [5, 6], see Scheme 1. Extra-pure grade Li salts ($LiClO_4$, $LiBF_4$, $LiPF_6$ and $LiCF_3SO_3$) were dissolved in poly(ethylene glycol)dimethylether (PEG) and propylene carbonate (PC) to 1 M solutions, which were blended with the mixed monomers, 1a+1b, in a prescribed ratio. The UV irradiation of the resulting mixed solutions yielded flexible films of the polymeric electrolytes. The compositions of the PMMA-based electrolytes are represented as PEO–PMMA/PEG–LiX/PC–LiX ($x/y/z$), where X denotes the anion of the salt, and x, y and z mean wt.% of each component.

The PMS-based polymer was prepared from a mixture of prepolymers, poly(3-carboxypropylmethylsiloxane-co-methylsiloxane) (2a), poly[dodeca(oxyethylene) propylmethylsiloxane] (2b), and poly(ethylene glycol) monomethylether (2c) [7]. 'Double-ion type' electrolytes were synthesized by polycondensation of the mixed prepolymer dissolving Li salts. The molar ratio of 2a:2b:2c was 1:6.6:6.5, in which the amount of COOH in 2a was equivalent to that of OH in 2b and 2c. The ratio of (Li)/(ethylene oxide unit) was 0.025. A 'single-ion type' electrolyte was obtained from the same prepolymers but containing LiOH. The molar ratio of 2a:2b:2c:LiOH was 1:4.4:4.3:6.4. In this case, the amount of COOH in 2a was equivalent to the total amounts of OH in 2b, 2c and LiOH [7].

The conductivity of the electrolyte was measured by an a.c. impedance meter at 10 kHz. A three-electrode type cell equipped with a Li reference and a Li counterelectrode was used for the polarization measurements of the Li electrode in the polymeric electrolytes [6, 7].

Results and discussion

PMMA-based electrolytes

Figure 1 shows typical temperature dependences of the ionic conductivity on the PMMA-based electrolytes. The specific conductivity of $LiClO_4$ in the PEO–PMMA matrix without PEG nor PC was about 10^{-5} S cm^{-1} at 30 °C [5]. Addition of PEG and/or PC to the polymer was effective for improving the conductance of the complex. Ionic conduction in the composite is mainly based on the interaction between Li$^+$
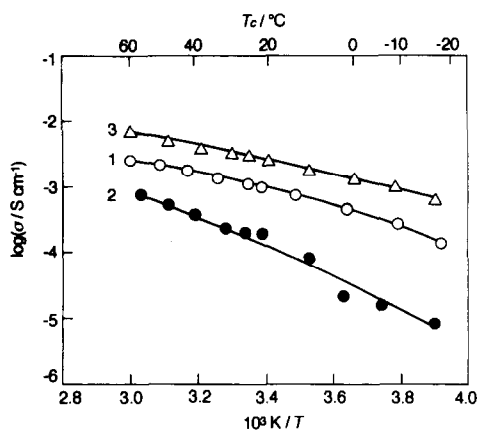
Fig. 1. Temperature dependence of the conductivity for PEO-PMMA/PEG-LiClO$_4$/PC-LiClO$_4$ (30/10/60) complexes: (1) without heat treatment; (2) after heating (100 °C, 24 h), and (3) treated by PC–LiClO$_4$ (1.0 M) after (2).
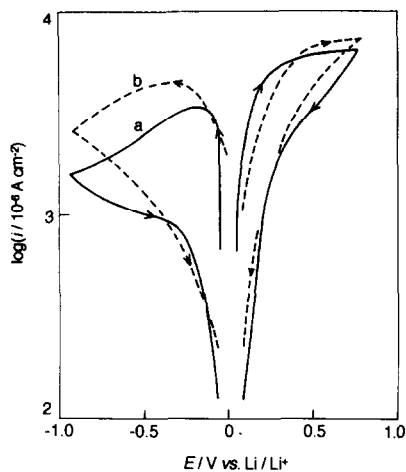
Fig. 2. Polarization curves of lithium electrode in PEO–PMMA/PEG–LiClO$_4$/PC–LiClO$_4$ (30/ 10/60) complexes: (a) treated by PC–LiClO$_4$ (1.0 M) after heating (100 °C, 24 h), and (b) without heat treatment.

and the ethylene oxide (EO) units in the side chain of the matrix polymer and PEG incorporated in the complex. The PEO–PMMA/PEG–LiClO$_4$/PC–LiClO$_4$ complex was heated at 100 °C for 24 h to eliminate water which had been incorporated in the composite during the film preparation. The ionic conductance of the composite was lowered by the heat treatment (Fig. 1, curve 2). This was because that the polymer matrix was hardened by thermal cross-linking among the unreacted double bonds in the main chains. The ionic conductivity of the heat-treated complex increased again after immersing it in the PC–LiClO$_4$ (1.0 M) solution (Fig. 1, curve 3). This treatment by PC–LiClO$_4$ is probably effective to plasticize the polymer matrix and to increase the carrier (ion) concentration in the complex. The high conductivity of the PC–LiClO$_4$-treated complex, $\sim 5 \times 10^{-3}$ S cm^{-1} at ambient temperature, gives great promise of practical utilization of this system.

Steady-state polarization curves of the Li negative electrode in PMMA-based electrolytes are shown in Fig. 2. The measurement was carried out potentiostatically [6]. The current densities in this work were represented by the values with respect to unit apparent surface area of Li in contact with the polymeric electrolyte. The current after potentiostating for 2 min at each preset potential was regarded as a quasi-steady-state value in this experiment. The potentials shown in Fig. 2 are IR-corrected. The polarization curves of Li in the PMMA-based electrolytes gave asymmetrical forms, which is fairly different from those observed in liquid electrolytes. A current hysteresis appeared in every case, especially in the cathodic branch. The limiting current for anodic polarization was about 5 mA cm^{-2}. However, the cathodic limiting current was much lower than that for anodic polarization. These are probably because of a change in the electrolyte concentration, especially Li$^+$ ion concentration, at the Li electrode/polymeric electrolyte interface under the highly polarized conditions. The PC–LiClO$_4$ treatment after 24 h heating (Fig. 2, curve a) contributed to decreasing

the polarization at the vicinity of the reversible potential. This suggests that the treatment is effective to improve the electrochemical interface structure. However, the PC–LiClO$_4$ treatment did not show any positive effect in the highly polarized potential regions.

PMS-based electrolytes

Figure 3 shows the temperature dependence of ionic conductivity for the PMS-based electrolytes, in which no liquid component is contained as a plasticizer. The 'double-ion' type electrolytes, PMS–LiClO$_4$ and PMS–LiCF$_3$SO$_3$, showed relatively high conductivities compared with those of conventional plasticizer-free PEO-based electrolytes. The ionic conductivity of the 'single-ion' type electrolyte, PMS–Li, was much lower than those of the 'double-ion' type electrolytes. The ionic transport number was measured by an ITIC (isothermal transient ionic current) method [8]. The transport number of Li$^+$, t_{Li^+}, in PMS–LiClO$_4$ was 0.53 ± 0.03 at room temperature. However, t_{Li^+} in PMS–Li was 0.98. These results indicate that only the Li$^+$ ion transfers in PMS–Li ('single-ion' type) whereas both the Li$^+$ ion and the counter anion move in 'double-ion' type complexes. The difference in t_{Li^+} between 'single-ion' type and 'double-ion' type complexes is essentially based on the difference in the combination ratio of the function groups in the prepolymers. In the 'double-ion' type complexes, all of the COOH groups in the prepolymer 2a form ester bonds with the OH groups in the prepolymers 2b and 2c. The ionic conductivity is exhibited as a result of dissociation of the dissolved Li salts in the complex. On the other hand, in the 'single-ion' type PMS–Li, the amount of COOH group in 2a was equivalent to the total amounts of OH groups not only in 2b and 2c but also in LiOH added. In other words, the counter anion in the 'single-ion' type electrolyte is the immobilized COO$^-$ anion in the prepolymer 2a.

Steady-state polarization curves were measured for the Li electrode in the PMS-based electrolytes. Figure 4 shows the Li polarization curves in 'double-ion' type PMS–LiClO$_4$ and 'single-ion' type PMS–Li. A current hysteresis was observed in PMS–LiClO$_4$, similarly to the cases of PMMA-based electrolytes. In the 'double-ion'
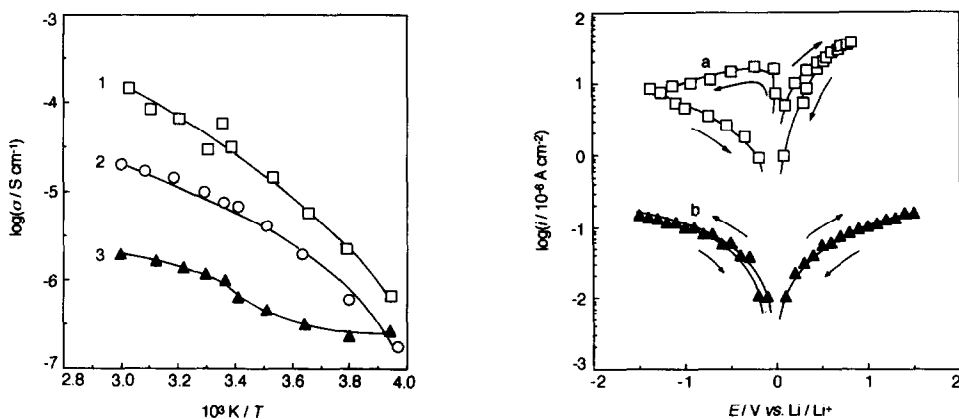

Fig. 3. Temperature dependence of the conductivity for PMS-based electrolytes: (1) PMS–LiClO$_4$; (2) PMS–LiCF$_3$SO$_3$, and (3) PMS–Li ('single-ion' type).

Fig. 4. Polarization curves of lithium electrode in PMS-based electrolytes: (a) PMS–LiClO$_4$, and PMS–Li ('single-ion' type).

type complexes, not only Li^+ cation but also the counter anion are transferred during the Faradaic current flowing. Thus, for the cathodic polarization, both cation and anion concentration at the Li electrode/polymeric electrolyte interface decreases with polarization time. This concentration change at the interface would cause the current hysteresis in the polarization curve, especially for the cathodic branch. On the other hand, the polarization curve measured in 'single-ion' type PMS–Li showed no current hysteresis and a symmetrical form for the anodic and cathodic branches although the limiting currents were rather low compared with those observed in 'double-ion' type PMS–LiClO$_4$. The high value of t_{Li^+} in PMS–Li would mainly contribute to this polarization behavior. As the anion is immobilized at the polymer matrix, the ionic conductivity and hence the limiting current density are rather low, compared with those in the 'double-ion' type complexes. However, there is no depression in the anion concentration at the interface between the Li electrode and the 'single-ion' type complex. This would be a major cause that no current hysteresis was observed for the Li polarization curve in the 'single-ion' type PMS–Li. Such polymeric solid electrolytes with high Li^+ transport numbers as PMS–Li will be advantageous to practical application. Especially, high performance electrochemical devices that are accompanied by cation transfer during their operation, e.g., a rechargeable Li battery and an electrochromic display, need excellent electrochemical properties at the solid electrode/solid electrolyte interface.

Acknowledgement

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