Short communication

Electrochemical properties of amorphous comb-shaped composite PEO polymer electrolyte

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Abstract

The electrochemical behaviour of a polyethylene oxide (PEO)-based composite polymer electrolyte are studied. The crystallinity of the PEO is suppressed by using a comb-shaped polymer to improve polymer chain mobility. An amorphous comb-shaped polymer, 'TEC-24', with a side-chain content of 24 mol%, is designed and fine silica powder is dispersed within it to enhance the mechanical properties above the melting point. The composite polymer electrolyte has an ionic conductivity of 1.6×10^{-4} and 1.6×10^{-3} S cm^{-1} at 30 and 90 °C, respectively, with an electrochemical stability window close to 5.0 V, even at 80 °C (versus Li/Li^{+}). The polymer electrolyte is evaluated using CuS as a cathode material and shows better cycle performance than that obtained with a liquid electrolyte.
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1. Introduction

Lithium batteries with liquid electrolytes can experience several problems such as leakage, safety, side-reactions and dissolution of electrode materials. These disadvantages can be avoided by using solid-state polymer electrolytes [1–3]. Although polyethylene oxide (PEO), as an elastomeric polymer, has been the subject of much attention [1–6], it has low conductivity due to its crystalline nature [4–7].

One of the methods to obtain a highly conductive PEO polymer electrolyte is to decrease the crystallinity of the oxyethylene segments by the introduction of side-chains to the PEO main chain [4,5,7–11]. In addition, side-chains promote the solvating of a salt [4,5]. Watanabe and co-workers [7–9] studied the concept of coupling ionic motion with side-chain motion that is characterised by a relatively short relaxation time compared with that of main-chain motion [7–9]. They designed a new comb-shape polyether host, viz., polyglycidylether, with short polyether side-chains [7]. It was found that the mechanical properties of the comb-shape polyether host were degraded as the number of side-chains was increased [5,8]. To improve the mechanical strength of the comb-shape polyether host, Ikeda et al.

[5,10] designed comb-shaped polymers of higher molecular weight with side-chains of trioxyethylene, TEC. Result showed that the conductivity of TEC-18, with a side-chain of 18 mol%, was 1.5×10^{-4} and 1.4×10^{-3} S cm^{-1} at 40 and 80 °C, respectively, with good mechanical properties [5]. The XRD pattern of the comb-shaped polymer TEC-18 shows crystalline peaks at room temperature [5].

The other promising method to improve conductivity is the use of inorganic fillers blended into the polymer electrolyte [6,12,13]. In a composite polymer electrolyte, the filler provides a support matrix so as to retain an overall solid structure, even at high temperature. It has been reported that the addition of finely dispersed ceramic powders greatly improves not only the mechanical stability, but also the electrochemical properties of polymer electrolytes.

The decomposition or dissolution of electrode materials in liquid electrolytes deteriorates battery performance [14–16]. Takada et al. [16] reported that solid electrolytes suppress the dissolution of electrode materials (LiVS$_2$, Li$_2$FeS$_2$, and Li$_2$FeCl$_4$) and thereby give excellent cell performance [16]. For a Li–CuS cell, the dissolution of the sulfide electrode material in liquid electrolyte (1 M LiPF$_6$/EC–2EMC) is one of the main reasons for poor cycleability [14].

In this paper, efforts are focused on suppression of the crystallity of a comb-shaped PEO based polymer to improve polymer chain mobility. An amorphous comb-shaped

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polymer, 'TEC-24', with a dispersion of fine SiO_2 powder, is designed to achieve an electrolyte with both high ionic conductivity and good mechanical stability. The electrochemical properties of the composite electrolyte are evaluated and tested with CuS as a cathode material.

2. Experimental

The starting material, 1,2-epoxy-4,7,10,13-tetraoxatetradecane (ETT-3) was synthesised from epichlorohydrin and triethylene glycol monomethylether in a manner similar to the synthesis of 1,2-epoxy-4,7,10-trioxaundecane [4,7–11]. The high molecular weight comb-shaped copolymer, 'TEC-24', with a side-chain content of 24 mol%, was obtained by co-ordinating anionic polymerisation of ethylene oxide (EO) with 1,2-epoxy-4,7,10,13-tetraoxatetradecane (ETT-3) using a Vandenberg-type catalyst at room temperature [4,5,8–10]. For comparison, 'TEC-12' was also synthesised. All the samples were distilled several times under a highly reduced pressure to obtain high-purity forms. The chemical structures of ETT-3 and TEC samples were confirmed by ^{13}C-NMR (GE-300 of General Electric Co. Ltd.) and ^{1}H-NMR (JEOL-JNM-GSX-270) [5,10]. The compositions of TEC polymers were determined from the integral ratio of methylene protons of the oxyethylene segments and the methyl protons of the side segments in the ^{1}H-NMR spectra by confirming methyl protons of the methoxy group (δ = ca. 3.2 ppm), and methylene and methane protons of the oxyethylene units (δ = ca. 3.4–3.8 ppm), respectively [5].

The thermal properties of the polymer matrix and polymer electrolyte were studied by means of differential scanning calorimetry (DSC; TA Instruments: 3100) under a nitrogen atmosphere. The sample was cooled to $-100\ ^{\circ}$C and heated to $100\ ^{\circ}$C at a rate of $10\ ^{\circ}$C min^{-1}, and the second measurement was carried out in the same way as the first measurement [5,7]. Thermal data were taken from the second scan measurement. The crystallinity of the polymer and the polymer electrolyte were studied by X-ray diffraction (XRD, Rigaku, Geigerflex D/Max-IIIC) at room temperature [5].

The ionic conductivities of the electrolyte and the stability of the electrode|electrolyte interface were determined by ac impedance spectroscopy with a Solartron 1260 frequency response analyser. A stainless-steel plate was used as a blocking electrode. The electrochemical stability of the electrolyte was investigated by linear sweep voltammetry with a EG&G 273 potentiostat at a scan rate of 10 mV s^{-1} [6,13,16].

The electrochemical compatibility of the electrolyte was tested with CuS as a cathode material [14,17,18].

3. Results and discussion

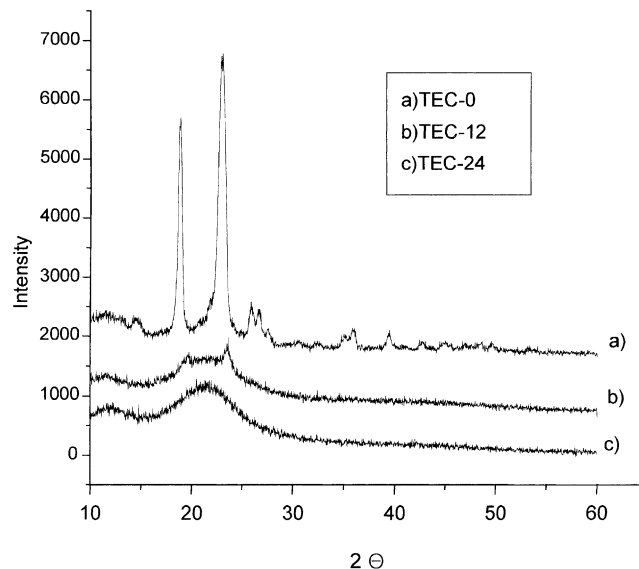The XRD patterns of PEO ('TEC-0', 'TEC-12', and 'TEC-24') at room temperature are shown in Fig. 1. The

Fig. 1. XRD patterns of PEO (TEC) as a function of side-chain content at room temperature.

pattern for TEC-0 is a typical XRD pattern for crystalline PEO. As the side-chain content increases, the intensity of the diffraction peaks becomes weaker and 'TEC-24' shows no sharp crystalline peaks even at room temperature, which indicates an amorphous nature.

Differential scanning calorimeter curves for PEO are presented in Fig. 2. From the DSC curves, glass-transition temperature (T_g) for 'TEC-24', 'TEC-12', and 'TEC-0' without Li salt is -70.1, -68.9 and $-59.3\ ^{\circ}$C, respectively. Above room temperature, the melting points, T_m, of 'TEC-0'
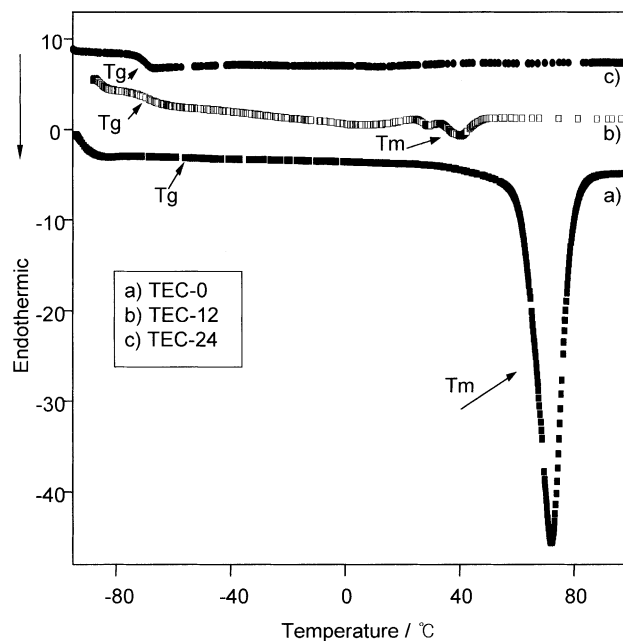

Fig. 2. DSC thermograms of PEOs (TEC) as a function of side-chain at a scan rate of $10\ ^{\circ}$C min^{-1}.
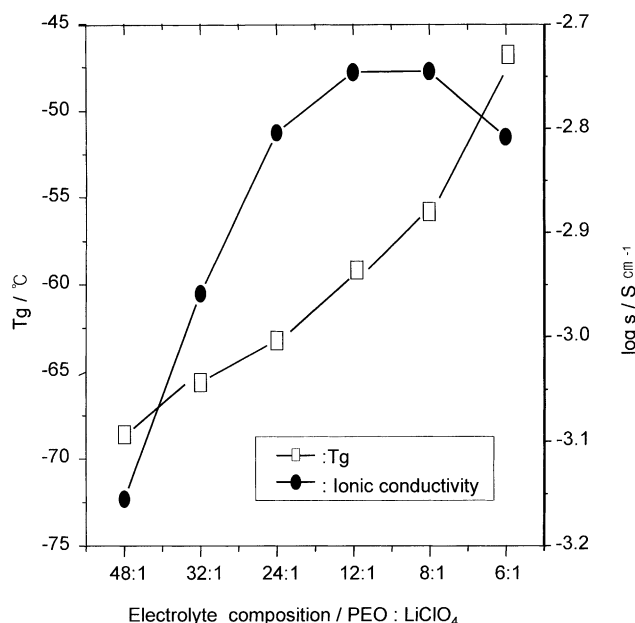
Fig. 3. Relationship between T_g and ionic conductivity as a function of Li salt concentration in polymer electrolyte at 80 °C.

Fig. 4. Arrhenius plots for composite polymer electrolyte for different polymer matrices.

and 'TEC-12' are 64.3 and 39.7 °C, respectively, which are attributed to melting of the crystalline part of the polymers. A small melting peak is also detected at 32.5 °C which indicates a semi-crystalline nature for 'TEC-12' [5]. By contrast, amorphous PEO, 'TEC-24', does not exhibit any melting peaks. As can be seen in Fig. 2, the introduction of side-chains results in not only a lowering of both T_g and T_m of comb-shaped polymers (amorphous and semi-crystalline), but also a lowering of the heat of fusion on melting. These results indicate that the mobility of segments in the comb-shaped polymer is higher than that in 'TEC-0'. and can enhance the ionic conductivity.

The glass-transition temperatures based on the DSC thermograms for 'TEC-24' and the corresponding ionic conductivities of the polymer electrolytes with variation of Li salt (LiClO$_4$) concentration are presented in Fig. 3. The TEC:Li ratio varies between 48:1 and 6:1. The T_g of the polymer electrolyte increases with increase in Li salt concentration since the interaction between polymer and salt is stronger at high Li salt concentrations than that at dilute concentration [5]. Also, the ionic conductivity increases with increase in Li salt concentration, as expected, but further increase in Li salt concentration above a ratio of 8:1 cause a decrease in ionic conductivity due to the crystalline nature of the PEO polymer electrolyte.

Since preliminary studies showed that the optimum concentration of the inorganic filler is 10 wt.% to give the highest Li ion conductivity with good mechanical properties, the filler concentration was fixed at this value in all the following experiments. The temperature dependence of ionic conductivity of the composite polymer electrolyte doped with LiClO$_4$ (PEO:Li = 12:1) with variation of side-chain concentration in PEO is shown in Fig. 4. The
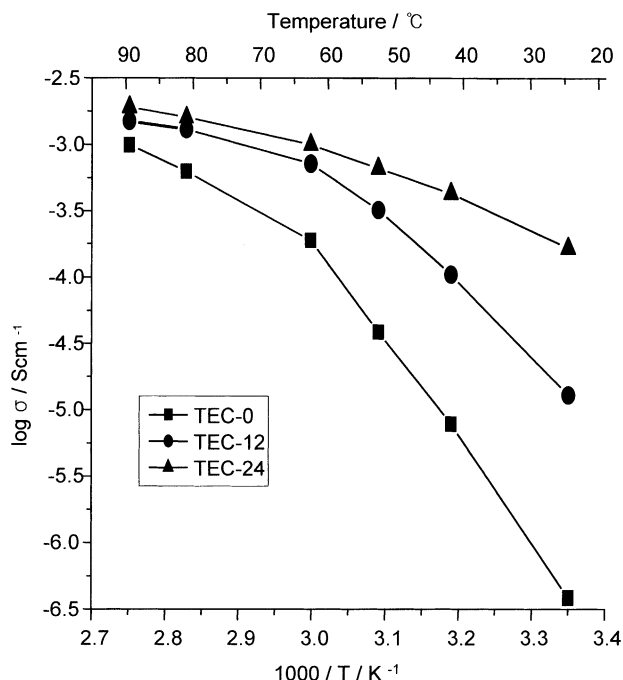
convex curved profiles above T_m are in accord with the general temperature dependence of most amorphous polymer electrolytes [1,2,5]. As expected from DSC data, the electrolyte with 'TEC-24' shows a high ionic conductivity of 1.6×10^{-3} and 1.6×10^{-4} S cm^{-1} at 90 and 30 °C, respectively, whereas 'TEC-0' shows a low ionic conductivity with a relatively high temperature dependence. The introduction of trioxyethylene segments as side-chains to the PEO main chain appears to influence not only the segmental motion but also the dissociation of Li salt in the matrix of oxyethylene segments to produce a high ionic conductivity in the amorphous polymer electrolyte [5,7,8].
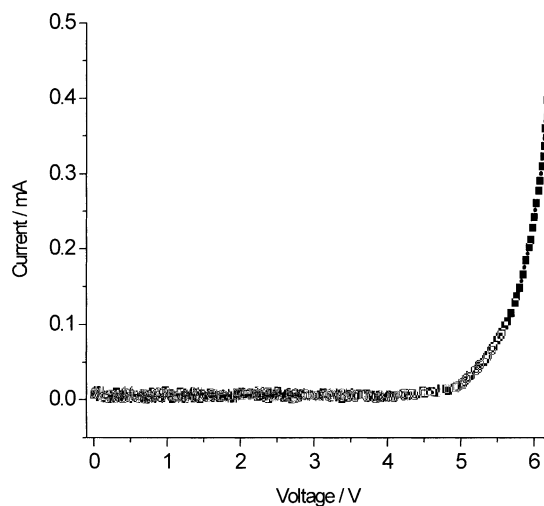

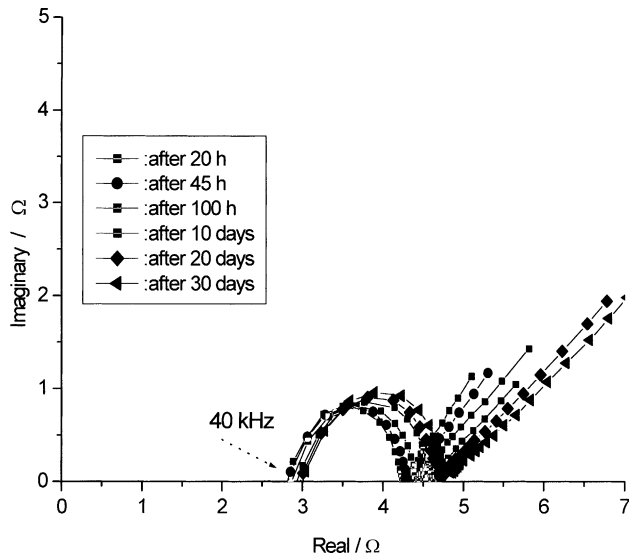Fig. 5. Electrochemical window of composite polymer electrolyte at 80 °C.

Fig. 6. Impedance responses of composite electrolyte|electrode interface at 90 °C under open-circuit conditions as a function of storage time (frequency range: 60 kHz–10 mHz).

Fig. 8. Comparison of cycling behaviour of CuS electrode in liquid electrolyte and solid composite polymer electrolyte.

The electrochemical stability of the composite polymer electrolyte was measured by linear sweep voltammetry at 80 °C. The results are shown in Fig. 5. The cell consisted of a polished stainless-steel (SS) counter electrode and a lithium a reference electrode, i.e. as Li|('TEC-24')$_{12}$ LiClO$_4$+ 10 wt.% SiO$_2$|SS. During the positive-going scan, oxidation starts to take place above 4.7 V (versus Li/Li$^+$). This indicates excellent electrochemical stability over a large voltage range, which allows the electrolyte to be used for lithium batteries. Also, the long-term stability of the lithium|electrolyte interface was tested with an ac impedance technique, since this parameters is important in terms of battery cycle-life and storage. The time dependency of the
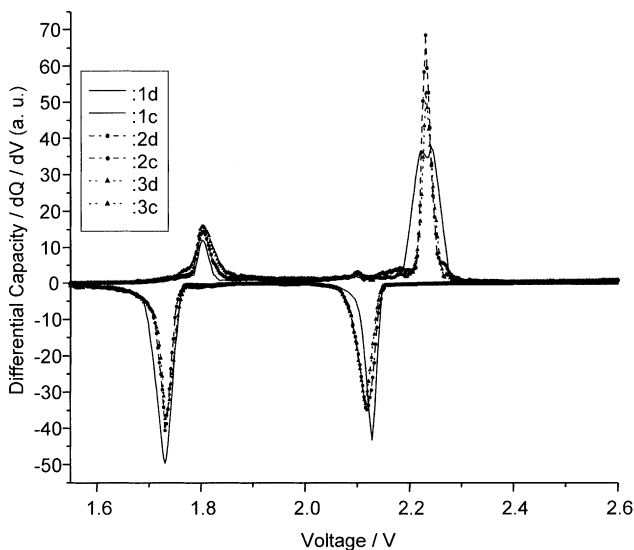

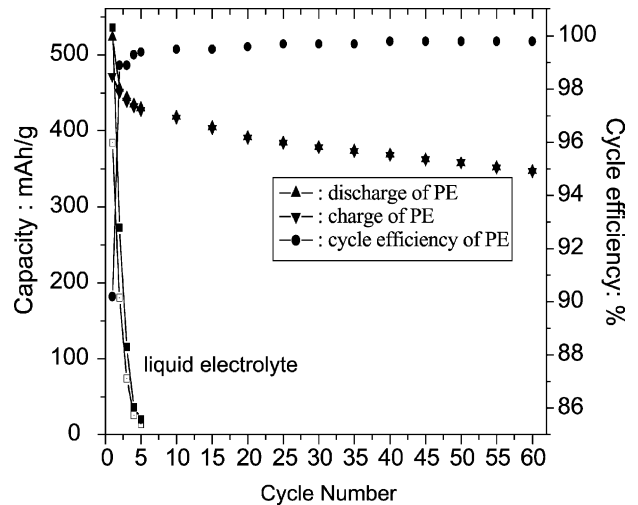Fig. 7. Cyclic voltammograms of CuS cathode at 90 °C between 1.55 and 2.6 V.

impedance spectra of Li|('TEC-24')$_{12}$LiClO$_4$ 10 wt.% SiO$_2$ Li cells are presented in Fig. 6. The interfacial resistance is very low, i.e. less than 20 Ω cm^{-2}, even after 40 days at 90 °C. This demonstrates that the Li electrode|electrolyte interface has a very high stability.

The compatibility of the composite polymer electrolyte was evaluated using CuS as a cathode material. As discussed previously [14], CuS has a high energy capacity, but its cycleability in liquid electrolyte is very poor. This is due to the formation of soluble product (Li$_x$S) and the irreversibility of the final product formed (metallic Cu) after discharge. Cyclic voltrammograms obtained between 1.55 and 2.6 V are shown in Fig. 7. The electrochemical behaviour of the CuS cathode in composite polymer is very much similar to that of in liquid electrolyte [14], but the decline in capacity is much less.

The capacity and cycle efficiency of a Li|CuS polymer cell at 90 °C are given in Fig. 8 for 60 cycles in the voltage range 1.55–2.6 V at 0.2 mA cm^{-2}. The capacity retention and cycle efficiency of the cell are far better compare with those of in a liquid electrolyte system. Even at the 60th cycle, the cell retains more than 60% of its initial capacity and sustains more than 98% cycle efficiency. Base on the above data, it is possible to enhance the cycle performance of the Li|CuS system by using a solid polymer electrolyte which suppresses sulfides dissolution during cycling.

4. Conclusions

An amorphous comb-shaped polymer 'TEC-24' has been designed to enhance the mobility of polymer chain, thereby, to increase the ionic conductivity by suppressing the crystallinity of PEO. Also, fine powders of SiO$_2$ have been blended

with the polymer electrolyte mainly to improve the mechanical property of the electrolyte above the melting point. The electrochemical properties of the composite polymer electrolyte are evaluated. 'TEC -24' has a low glass-transition temperature of $-70.1\,^{\circ}\mathrm{C}$ and a high ionic conductivity of $1.6 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at $90\,^{\circ}\mathrm{C}$. The compatibility of the composite polymer electrolyte has been tested using CuS as a cathode material, and shows better cycle performance and efficiency compared with those obtained with a liquid electrolyte.

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