Polymer electrolytes based on polyesters of thiodipropionic acid: 2. Electrochemical characterization

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Starting from aliphatic polyesters of thiodipropionic acid and linear glycols containing ethylene oxide groups, free-standing films of solid polymer electrolytes were prepared using a trifunctional crosslinking agent. The electrochemical characteristics of some of these new materials, including their performance in lithium batteries, are reported and discussed.

(Keywords: solid polymer electrolytes; thiodipropionic acid polyesters; lithium battery)

INTRODUCTION

A new series of aliphatic polyesters of thiodipropionic acid and linear glycols containing ethylene oxide groups have been prepared. These polymers, which at room temperature are highly viscous liquids, can easily dissolve $LiClO_4$, and the resulting semi-solid systems are of considerable interest as polymer electrolytes because at room temperature they show conductivity values greater than those of 'conventional' electrolytes based on poly(ethylene oxide) (PEO)[1]. In an effort to develop free-standing films, these materials were successfully crosslinked using a trifunctional crosslinking agent[2].

The present study reports the electrochemical characteristics of some of these new ionic conducting polymers with a view to battery applications. The effect of crosslinking on their electrochemical features is also examined, and their performance is discussed and compared to that of a 'conventional' PEO-based electrolyte.

EXPERIMENTAL

Polymer preparation

The polymer electrolytes examined were polyesters of thiodipropionic acid and triethylene glycol (PTDPA-EO(2)), with an amount of dissolved $LiClO_4$ corresponding to an (S + O)/Li molar ratio of 18 (PTDPA-EO(2)$_{18}$LiClO$_4$), and of thiodipropionic acid and pentaethylene glycol (PTDPA-EO(4)), with an (S + O)/Li molar ratio of 22 (PTDPA-EO(4)$_{22}$LiClO$_4$), prepared as in ref. 1. In the calculation of this (S + O)/Li molar ratio, all the atoms of sulfur and oxygen in the backbone, excluding the terminal groups and carbonyl oxygen, have been considered.

Crosslinking procedure

First, 1.0 g (0.65 OH meq) of (PTDPA-EO(2)$_{18}$LiClO$_4$) was dissolved in 10 ml of $CHCl_3$. To this solution were added 0.12 g (0.9 NCO meq) of the crosslinking agent Desmodur R (4,4′,4″-methylidine tris(phenylisocyanate) in butyl acetate and naphtha, a commercial product from Bayer) and 0.036 g of catalyst (dibutyltin dilaurate). The mixture was poured into a polytetrafluoroethylene (PTFE) flat container; the reaction leading to polyurethane crosslinking points was accomplished at room temperature under anhydrous atmosphere in 12 h, and the resulting transparent, rubber-like solid film, partly soluble in chlorinated solvents, had a thickness in the range of several hundred micrometres. The same procedure was used to crosslink the polymer without dissolved lithium salt. The crosslinked polymer films were then dried under vacuum at 60°C overnight.

Differential scanning calorimetry (d.s.c.) measurements

The glass transition temperature (T_g) of the materials was evaluated by differential scanning calorimetry with Perkin–Elmer DSC-7 at a heating rate of 20°C min^{-1} in the -80 to 100°C temperature range.

Frequency response analysis (f.r.a.) measurements

The electrochemical properties of the polymer electrolytes were evaluated by impedance spectroscopy using a 1255 Solartron frequency analyzer coupled to a 273 PAR potentiostat/galvanostat, both interfaced with a personal computer. The polarization voltage was 5 mV. The impedance results were examined by Boukamp's

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fitting program[3], where capacitances and Warburg impedances were replaced by constant-phase elements to account for deviation from ideal behaviour. Blocking cells with stainless-steel electrodes were used for conductivity measurements, and Li symmetrical non-blocking cells and Li batteries were used to investigate interface phenomena. The positive electrode of the lithium batteries was an electronically conducting polymer, i.e. poly(*N*-3,6-dioxaheptylpyrrole) (PNDP), electrosynthesized (12×10^{-7} monomer mol cm^{-2}) as in ref. 4, which has shown good cyclability features in lithium solid-state batteries with 'conventional' PEO-based polymer electrolytes; the batteries were potentiostatically charged up to 3.9 V before the f.r.a. measurements. All the cells were sealed in an Ar-filled glove box, and the electrode areas were 0.4 cm^2.

Cyclic voltammetry (c.v.)

The characteristics of Li cyclability in the polymer electrolytes, the anodic stability of these polymer electrolytes and the cyclability of Li/polymer electrolyte/PNDP batteries were investigated by cyclic voltammetry (c.v.) using a PAR potentiostat/galvanostat. The voltage scan rate was 50 mV s^{-1} and the temperature 70°C.

RESULTS AND DISCUSSION

Glass transition temperature

The T_g data of linear and crosslinked polymers are shown in *Table 1*. The crosslinking did not result in significant changes in T_g of the original polymer, and still less when $LiClO_4$ was dissolved in the initial polyesters.

Ionic conductivity

Figure 1 compares the conductivity values at various temperatures of linear PTDPA-EO(2)$_{18}$LiClO$_4$ and crosslinked PTDPA-EO(2)$_{18}$LiClO$_4$ to those of 'conventional' PEO$_{20}$LiClO$_4$. The crosslinking process does not significantly modify the polymer conductivity. At low temperature the polyester-based polymers show ionic conductivity that is higher than that of PEO$_{20}$LiClO$_4$ by two orders of magnitude. By contrast, at high temperatures, when PEO-based electrolytes melt, the conductivity of PEO$_{20}$LiClO$_4$ is higher, mainly because of a lower T_g that permits faster segmental motions.

Lithium cyclability

To test the viability of these new materials as polymer electrolytes in lithium batteries, we investigated by c.v. the lithium cyclability process $\mathrm{Li^+ + e^- \leftrightarrow Li}$. *Figure 2* shows the c.v. on Al electrodes of linear PTDPA-EO(4)$_{22}$LiClO$_4$ and crosslinked PTDPA-EO(2)$_{18}$LiClO$_4$. The shapes of the curves are very similar to those observed with cells using 'conventional' PEO-based electrolytes.

Table 1 T_g data for linear and crosslinked polymers

Sample	T_g (°C)
PDTPA-EO(2) linear	−42
PDTPA-EO(2) crosslinked	−34
PDTPA-EO(2)$_{18}$LiClO$_4$ linear	−28
PDTPA-EO(2)$_{18}$LiClO$_4$ crosslinked	−26

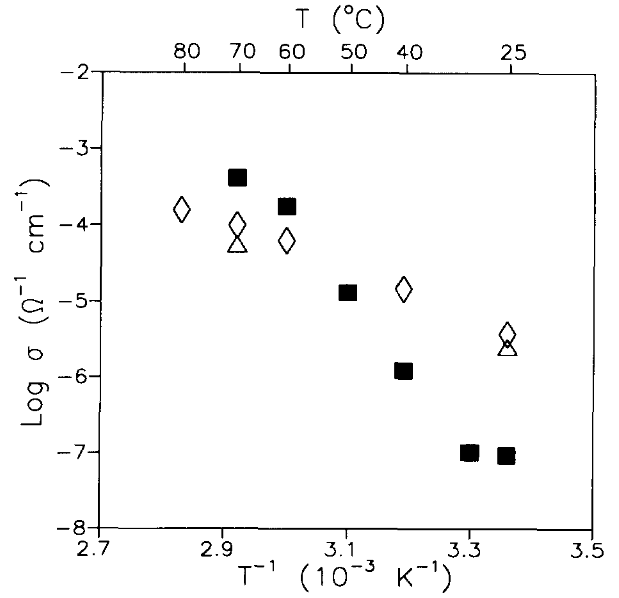

Figure 1 Ionic conductivity values from f.r.a. measurements with blocking electrodes: (◇) linear PTDPA-EO(2)$_{18}$LiClO$_4$; (△) crosslinked PTDPA-EO(2)$_{18}$LiClO$_4$; (■) PEO$_{20}$LiClO$_4$

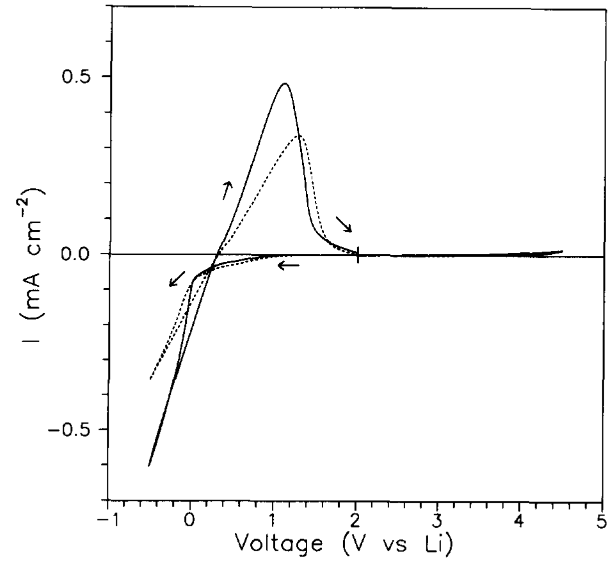

Figure 2 Cyclic voltammograms (c.v.) on Al electrode at 50 mV s^{-1} and at 70°C of PTDPA-EO(4)$_{22}$LiClO$_4$ (——) and of crosslinked PTDPA-EO(2)$_{18}$LiClO$_4$ (·····) polymer electrolytes; Li counter-electrodes

The well defined anodic peak of lithium stripping during the anodic scan, with high Coulombic efficiency (Q_{ox}/Q_{red} ca. 90%), demonstrates that the lithium cyclability in these materials is good. In addition, the c.v. show a wide range of electrochemical stability, i.e. the wide electrochemical window of these polymer electrolytes; no electrochemical reactions occur at positive potentials greater than that of the lithium stripping up to 4.5 V. Note that the c.v. of the linear and crosslinked electrolytes are similar, indicating that the crosslinking process has no significant effect on the electrochemical performance of these new polymer electrolytes.

Lithium/polymer electrolyte interface

In order to evaluate the charge-transfer resistance of the Li deposition–stripping process on the lithium itself,

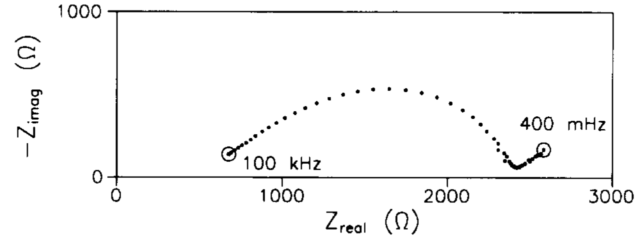

Figure 3 F.r.a. spectrum of Li/PTDPA-EO(2)$_{18}$LiClO$_4$/Li cell at 70°C (crosslinked polymer electrolyte thickness of ca. 200 μm)

Table 2 Circuit parameters of Li/PTDPA-EO(2)$_{18}$LiClO$_4$/Li cell at 70°C from impedance data of *Figure 3*

R_b (Ω)	800
R_{ct} (Ω)	1600
C_{dl} (μF)	0.6

impedance spectra at 70°C were carried out using Li symmetrical cells. *Figure 3* shows the f.r.a. spectrum of the cell with crosslinked PTDPA-EO(2)$_{18}$LiClO$_4$. In the examined frequency range the spectrum shows the semicircle related to the electrode/electrolyte interface process, followed by a 45° Warburg line, which is representative of a mass-transport process under semi-infinite diffusion conditions. The cell circuit parameters, i.e. bulk resistance (R_b), charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}), determined by a fitting program on the basis of a modified Randles equivalent circuit are reported in *Table 2*.

Lithium–polymer battery

The performance of the crosslinked PTDPA-EO(2)$_{18}$ LiClO$_4$ was also tested in a Li/PTDPA-EO(2)$_{18}$LiClO$_4$/ PNDP battery. Shown in *Figure 4*, the f.r.a. spectrum of this battery at 70°C shows the semicircle related to the electrode/electrolyte interface processes, followed by a 45° inclined Warburg line and, at very low frequency, a spike, which is representative of a capacitive behaviour associated with the mass-transport process in finite-thickness conditions.

The spectrum was interpreted on the basis of a modified Randles equivalent circuit[5], where the diffusion-controlled zone is represented by three elements: the Warburg impedance ($Z_W = A_W\omega^{-1/2} - jA_W\omega^{-1/2}$) for the semi-infinite condition, the limiting resistance (R_L) and the capacitance (C_L) for the finite-thickness condition; the fitting data are shown in *Table 3*. By subtracting the R_{ct} value of the Li/PTDPA-EO(2)$_{18}$LiClO$_4$ interface from the battery R_{ct} value, the charge-transfer resistance at the PTDPA-EO(2)$_{18}$LiClO$_4$/PNDP interface was roughly estimated to be 500 Ω. The elements A_W, R_L and C_L were used to calculate the apparent diffusion coefficient of the charge-balancing ions in the polymer electrode (D_{app}) by the relation $D_{app} = l^2/(3R_LC_L)$ where 1 μm is the PNDP film thickness value. *Table 3* lists the D_{app} value as well as the value of the parameter $P = 2A_W^2C_L/(3R_L)$, which for the theoretical model[5] has to equal 1, in order to represent the consistency of the experimental data. The D_{app} values are almost the same as that previously determined from f.r.a. spectra of Li/PNDP batteries with PEO-based electrolyte in ref. 6. The comparison of the spectra in *Figures 3* and *4* clearly demonstrates that the Warburg impedance due to transport in the polymer electrolyte is

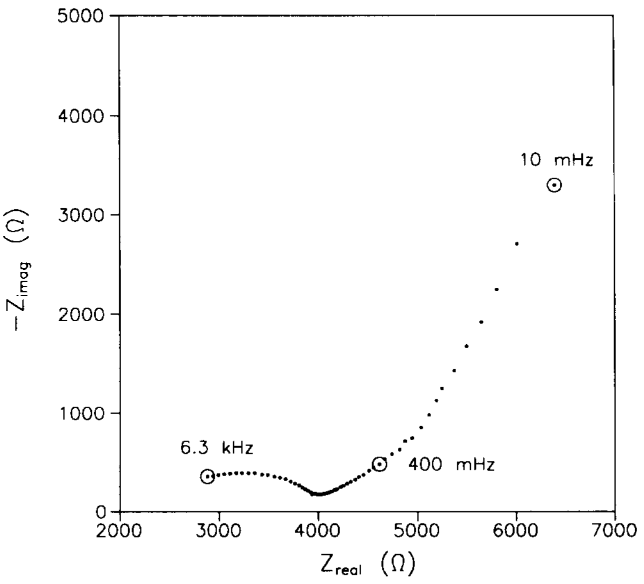

Figure 4 F.r.a. spectra of Li/PTDPA-EO(2)$_{18}$LiClO$_4$/PNDP cell at 70°C charged up to 3.9 with 21 mC cm^{-2} (crosslinked polymer electrolyte thickness of ca. 500 μm)

Table 3 Circuit parameters of Li/PTDPA-EO(2)$_{18}$LiClO$_4$/PNDP cell at 70°C from impedance data of *Figure 4*

R_b (Ω)	2600
R_{ct} (Ω)	1300
C_{dl} (μF)	2.0
A_W ($\Omega^{-1/2}$ s$^{-1/2}$)	870
C_l (mF)	1.4
R_l (Ω)	600
P	1.2
D_{app} (cm^2 s^{-1})	4×10^{-9}

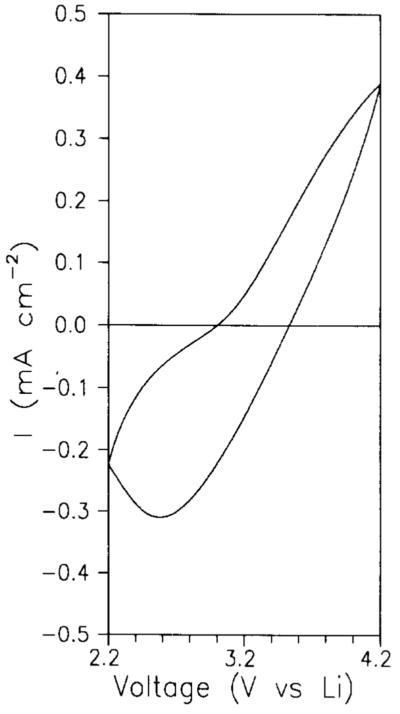

Figure 5 Tenth c.v. of Li/PTDPA-EO(2)$_{18}$LiClO$_4$/PNDP cell at 50 mV s^{-1} and 70°C; Q_{charge} = 7 mC cm^{-2}; Coulombic efficiency 99% (crosslinked polymer electrolyte thickness of ca. 500 μm)

less important than that due to transport in the polymer electrode in these Li batteries.

The cyclability performance of the Li/PTDPA-EO(2)$_{18}$LiClO$_4$/PNDP battery was also tested by c.v. at 70°C (*Figure 5*). The cyclable charge during c.v. appears lower at the same sweep rate than that reported in ref. 6 for Li/PNDP battery with PEO-based electrolyte, although when the Li/PTDPA-EO(2)$_{18}$LiClO$_4$/PNDP battery is potentiostatically charged the cell reaches almost the same level of charge (ca. 20 mC cm^{-2} at 3.9 V).

In our case the difference during c.v. is mainly due to the higher ohmic drop in the battery with crosslinked PTDPA-EO(2)$_{18}$LiClO$_4$ electrolyte because of the polymer electrolyte's greater thickness.

CONCLUSIONS

The reported findings show that crosslinked polyesters containing ethylene oxide and thiodipropionic acid moieties can be used as solid polymer electrolytes in lithium rechargeable batteries. Their high conductivities at room temperature, their low charge-transfer resistances at the lithium interface and their wide electrochemical window are promising features for use in thin-film battery technology, especially because these materials can be easily obtained in rubber-like form. Further study should be undertaken to investigate the long-term stability of both of these electrolytes and, in particular, of the lithium/polymer electrolyte interface.

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