

Electrochemical characterization of new conducting polymer electrolytes

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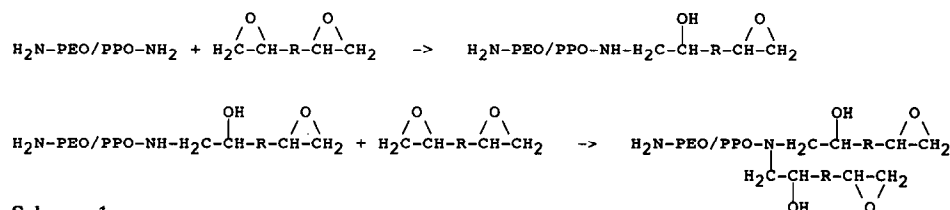
Abstract

Prepared with bis-amino PEO/PPO copolymers, with and without amino PEO oligomers, and the cross-linking agent butanediol diglycidyl ether, a new series of cross-linked polymer electrolytes were investigated for their ionic conductivity and for the electrochemical properties of lithium cycleability and lithium polymer electrolyte compatibility. Room-temperature conductivity was found to be two order of magnitude higher than that of 'conventional' PEO-based electrolytes; compatibility with metallic lithium proved to be fairly good.

Introduction

Given the technological importance of polymer electrolytes for solid-state rechargeable batteries and electrochromic devices, and the fact that the semicrystalline 'conventional' polyethylene oxide (PEO) electrolytes have unsuitable conductivity values, much work has been devoted to develop materials with high conductivity at room temperature. The main strategies to reduce the crystallinity of PEO-based electrolytes include the use of copolymers, cross-linkage and the modification of the macromolecule by pendent PEO segments [1].

Recently, cross-linked polymer electrolytes have been synthesized [2, 3]; the network basis is a copolymer of polyethers with two terminal primary amines and the cross-linkage, which results in a three-dimensional lattice, occurs by reaction of the amine groups with a diepoxy compound, as shown in Scheme 1.



Scheme 1.

The cross-linking process was carried out also in the presence of PEO oligomers with a terminal primary amine, that compete against diamine polyethers in the reaction with diepoxy compounds; the set of reactions produces a three-dimensional lattice with pendent PEO segments.

This paper reports and discusses, with a view to lithium-battery applications, the electrochemical characteristics of polymer networks obtained from diamine polyethers of different molecular weight, the cross-linkage being carried out both in absence and in presence of amino PEO oligomers. The performance of these polymer networks is also compared with that of a 'conventional' PEO electrolyte.

Experimental

Polymer network preparation

The polymer electrolytes were prepared from commercially-available bis-amino PEO/PPO copolymers (2000 and 6000 mol. wt. from Fluka and Texaco) and amino PEO oligomers (PEONH₂, synthesized from PEOOH 350 and 750 mol. wt., Aldrich); the cross-linking agent was butanediol diglycidyl ether (BDDGE, Aldrich 95%). Lithium perchlorate was dissolved in ethanol or in acetonitrile and mixed with bis-amino PEO/PPO copolymers; PEONH₂-enriched mixtures were also prepared. The cross-linking agent was added after solvent being evaporated. The ratio between total ether units and lithium was 21 and the epoxy/amine molar ratio without PEONH₂ was 2 and with it (PEONH₂/copolymer molar ratio 0.4) the BDDGE content was incremented by an equimolar amount. The mixture was poured on a Teflon plate in a glove box. The cross-linking reaction was thermally initiated at ~80 °C and occurred in a few minutes; the cross-linked polymer samples (thickness 100–400 μm) were then dried under primary vacuum at 100 °C for 15 h. The polymer electrolytes prepared from 6000 and 2000 mol. wt. PEO/PPO copolymers without amino PEO oligomers are hereinafter called I and II, those prepared from 2000 mol. wt. PEO/PPO in presence of 750 mol. wt. and 350 mol. wt. PEONH₂ are called III and IV, and those prepared from 6000 mol. wt. PEO/PPO with 750 mol. wt. and 350 mol. wt. PEONH₂ are called V and VI, respectively.

FRA measurements

Electrochemical properties of polymer electrolytes were evaluated by impedance spectroscopy using a 1255 Solartron frequency response analyzer coupled to a 273 PAR potentiogalvanostat, both interfaced with a personal computer; the a.c. polarization voltage was 5 mV. The impedance results were examined by Boukamp's fitting program [4], where capacitances and Warburg impedances were replaced by constant-phase elements to account for deviation from ideal behavior. Blocking cells with stainless-steel electrodes were used for conductivity measurements, and lithium symmetrical non-blocking cells were used to investigate interface phenomena. The electrode areas were 0.4 cm².

Cyclic voltammetry

The characteristics of lithium cycleability in polymer networks were investigated by cyclic voltammetry (CV) on aluminum electrodes and the electrochemical stability window of these polymer networks by CV on stainless-steel electrodes using lithium counter electrodes and with 273 PAR potentiogalvanostat.

Results and discussion

Ionic conductivity

Table 1 shows the conductivity data at 25 and 70 °C of I, II, III and IV polymer networks and, for comparison, the data of 'conventional' PEO₂₀/LiClO₄ polymer electrolyte. At room temperature the conductivity of all cross-linked polymers is higher than that of 'conventional' PEO electrolyte as expected for amorphous systems. On the other hand at 70 °C, when the 'conventional' PEO electrolyte is in the elastomeric state, the conductivity values of polymer electrolytes are almost comparable, with the exception of II. The low conductivity of II in comparison with that of I can be related to the higher cross-link degree of polymer network prepared from 2000 mol. wt. PEO/PPO copolymer; furthermore, the high conductivity of III and IV samples indicate that the cross-linking process of 2000 mol. wt. PEO/PPO copolymer in presence of amino PEO oligomers produces significantly less stiff polymer networks owing to the pendent PEO segments. However, it is worth noting that the cross-linking process of 6000 mol. wt. PEO/PPO copolymer both in presence and in absence of amino PEO oligomers produces polymer networks with almost the same conductivity values: 3×10^{-5} and $2 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ were evaluated at 25 °C for V and VI samples, respectively.

Lithium cycleability and polymer network stability

To test the feasibility of the polymer networks as polymer electrolytes in lithium batteries, we investigated the lithium cycleability process ($\text{Li}^+ + e^- \leftrightarrow \text{Li}$) by CV. Figure 1 shows IV sample's CV at 50 mV s⁻¹ and 70 °C on aluminum electrode. A well-defined anodic peak of lithium stripping (during the anodic sweep) with high coulombic efficiency ($Q_{\text{ox}}/Q_{\text{red}} \sim 90\%$) demonstrates that the lithium cycleability in polymer network is good. On the other hand Fig. 1 also shows the CV of 'conventional' PEO electrolyte; the shape of the CVs is almost the same, indicating that the cross-linking process has no significant effect on the electrochemical performances.

An important feature of a polymer electrolyte is its electrochemical stability in the anodic region; Fig. 2 shows IV sample's CV at 50 mV s⁻¹ and 70 °C on a stainless-steel electrode. The potential sweep can be extended over 5 V with respect to the lithium counter electrode without observing appreciable current, and a wide electrochemical stability window makes it suitable for use in many lithium-based batteries.

Lithium/polymer electrolyte interface

In order to evaluate the charge-transfer resistance of the lithium deposition-stripping process on lithium itself from the polymer networks, we carried out, at

TABLE 1

A.c. conductivity data at 25 and 70 °C

Sample	Conductivity	
	at 25 °C ($\Omega^{-1} \text{ cm}^{-1}$)	at 70 °C ($\Omega^{-1} \text{ cm}^{-1}$)
I	2×10^{-5}	2×10^{-4}
II	3×10^{-6}	5×10^{-5}
III	2×10^{-5}	3×10^{-4}
IV	2×10^{-5}	5×10^{-4}
PEO ₂₀ /LiClO ₄	1×10^{-7}	5×10^{-4}

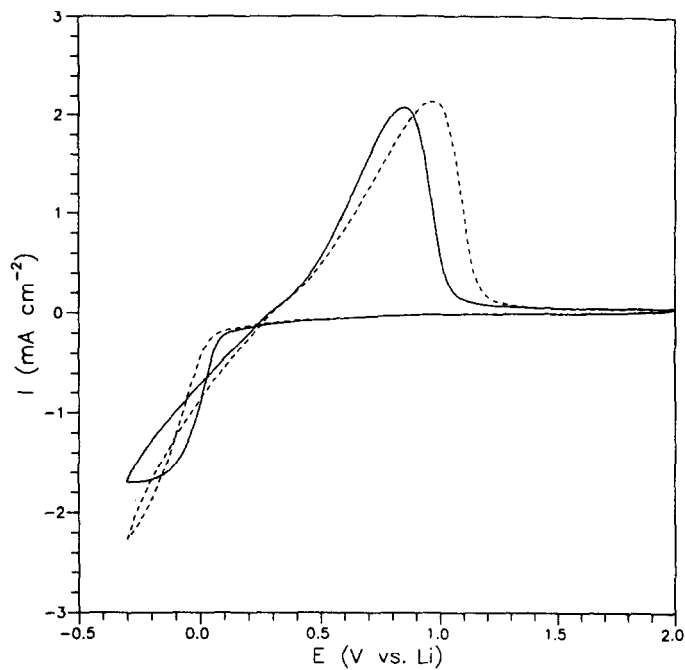


Fig. 1. Cyclic voltammograms at 50 mV s^{-1} and 70°C of (—) $\text{Li}^+ + e^- \leftrightarrow \text{Li}$ process of IV polymer network and (---) 'conventional' $\text{PEO}_{20}/\text{LiClO}_4$ on aluminum electrodes.

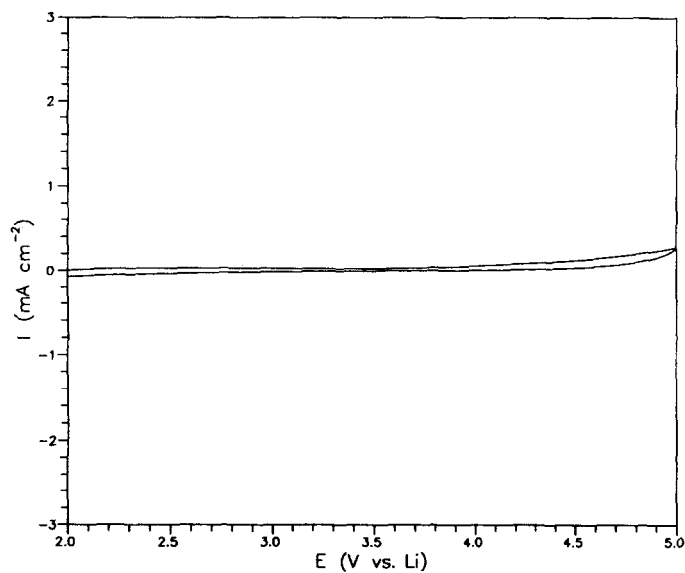


Fig. 2. Cyclic voltammograms at 50 mV s^{-1} and 70°C of IV polymer network on a stainless-steel electrode between 2 and 5 V vs. lithium.

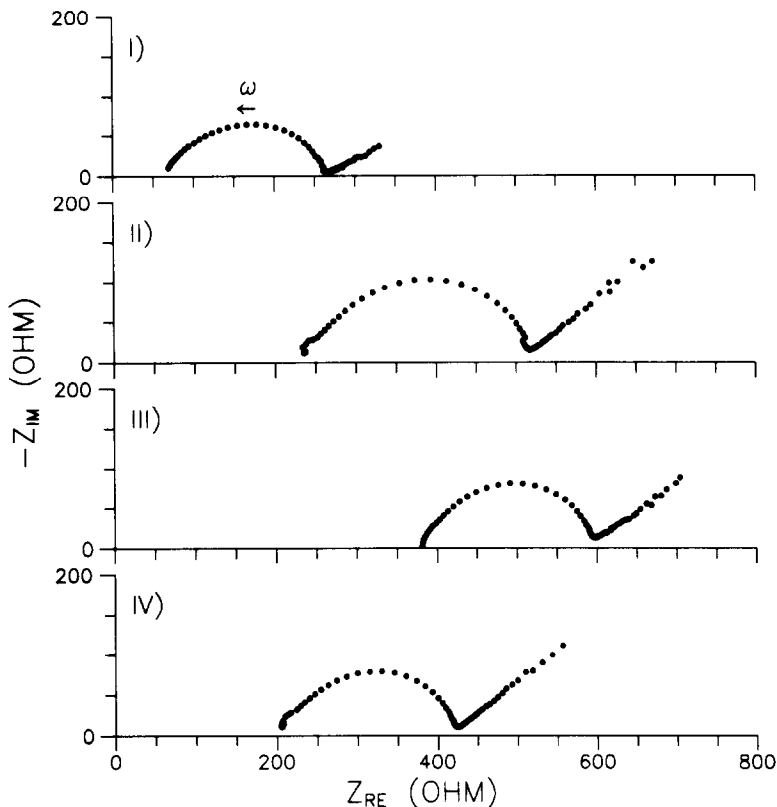


Fig. 3. Impedance spectra at 70 °C of lithium symmetrical cells 1 h after cell assembly with I, II, III and IV polymer electrolytes (polymer thickness ranging from 50 to 500 μm); frequency range: 100 kHz–0.013 Hz.

70 °C, impedance spectra using lithium symmetrical cells. Figure 3 shows the FRA spectra of the cells with I, II, III and IV polymer networks recorded 1 h after cell assembly. In the examined frequency range the spectra show the semicircle related to an electrode/electrolyte interface process, followed by a 45° Warburg line which represents 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 fitting program on the basis of a modified Randles equivalent circuit, are shown in Table 2.

The R_{ct} values of the lithium deposition-stripping process from these new polymer networks are almost comparable with each other and are comparable with the R_{ct} value (160 Ω) recorded using at the same temperature 'conventional' PEO₂₀/LiClO₄.

The compatibility of the polymer networks with lithium electrode was investigated by testing the characteristics of the symmetrical lithium cells at progressively longer storage times at 70 °C. Figure 4 shows the spectra of the cell with IV polymer network and Table 3 the circuit parameters. The results indicate a significant shift of the semicircle, whereas the R_{ct} value remains almost constant throughout storage time. Because no significant aging process occurs in the polymer network with stainless-

TABLE 2

Cell circuit parameters from impedance data of Fig. 3

Sample	R_b (Ω)	R_{ct} (Ω)	C_{dl} (μF)	A_w ($\Omega \text{ s}^{-1/2}$)
I	64	203	5.3	17
II	244	270	4.6	50
III	388	204	4.5	38
IV	215	205	3.4	40

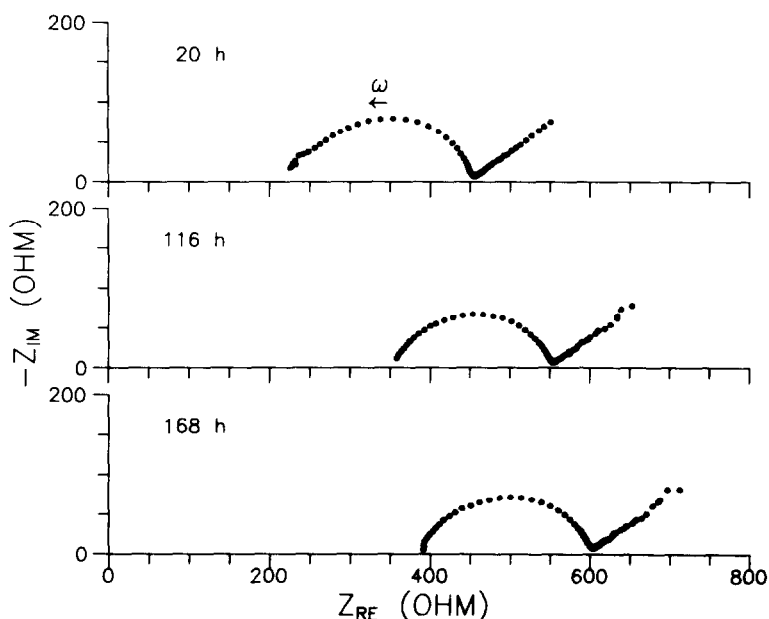


Fig. 4. Evolution of the impedance spectra of a lithium symmetrical cell with IV polymer network at progressively longer storage periods at 70 °C; frequency range: 100 kHz–0.013 Hz.

TABLE 3

Cell circuit parameters from impedance data of Fig. 4

Time (h)	R_b (Ω)	R_{ct} (Ω)	C_{dl} (μF)	A_w ($\Omega \text{ s}^{-1/2}$)
20	238	213	2.6	31
116	354	195	2.8	34
168	389	211	2.6	34

steel blocking cells as shown in Fig. 5, where impedance spectra over time are reported, the increasing of the high frequency intercept of the semicircle in Fig. 4 must be due to the formation of a resistive layer between the electrolyte and the lithium electrode;

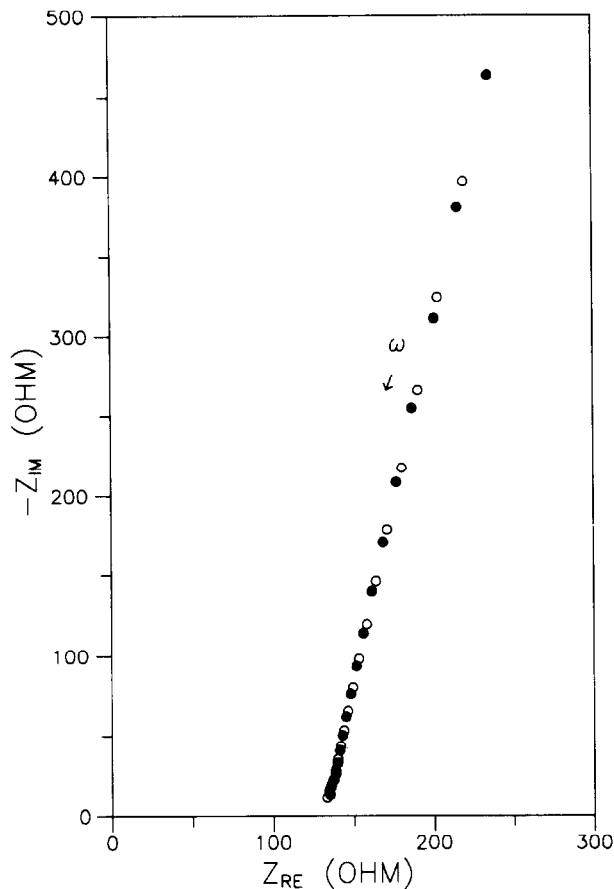


Fig. 5. Impedance spectra of a stainless-steel blocking cell with IV polymer network at progressively longer storage times at 70 °C: (●) 1 h, (○) 170 h; frequency range: 100 kHz–398 Hz.

this layer modifies cell-geometrical resistance without significantly affecting the charge-transfer process.

Conclusions

The polymer networks prepared using bis-amino 2000 mol. wt. PEO/PPO copolymer with amino PEO oligomers or 6000 mol. wt. copolymer even without PEO oligomers and the cross-linking agent butanediol diglycidyl ether, combine good mechanical properties and high conductivity at room temperature, ~ 2 orders of magnitude higher than that of 'conventional' PEO-based electrolytes. This is a promising feature for use in thin-film battery and electrochromic device technology taking into account too that these polymer networks are easy to prepare. The data also demonstrate that PEO-pendent groups enhance the conductivity of polymer network with higher cross-link degree only.

On the other hand, the electrochemical properties of lithium cycleability and lithium/polymer electrolyte interface of these new polymer network at 70 °C are almost comparable with those of 'conventional' PEO electrolytes.

Acknowledgements

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