Characteristics of a poly(ethylene oxide)–LiBF$_4$ polymer electrolyte

F. CROCE, R. CURINI, S. PANTALONI, S. PASSERINI, A. SELVAGGI, B. SCROSATI

Dipartimento di Chimica, Università di Roma, 'La Sapienza', Rome, Italy

The poly(ethylene oxide)–lithium tetrafluoborate complex, $(PEO)_7 LiBF_4$, has been characterized in terms of total and electronic conductivity, lithium transport number, stability versus lithium electrode and thermal properties. The results indicate that this polymeric electrolyte offers promises of application in lithium-based electrochemical devices.

1. Introduction

Many studies have been reported on complexes between poly(ethylene oxide) (PEO) and lithium salts [1, 2] since these materials may find application as thin-film, polymer electrolytes in versatile electrochemical devices [3–6].

Quite surprisingly, very few investigations have so far been reported on PEO complexes using lithium tetrafluoborate, LiBF$_4$, a salt which is commonly used for organic solvent solutions of interest in lithium batteries [7].

In this paper we report the characterization of a polymer electrolyte formed by poly(ethylene oxide) and lithium tetrafluoborate in the 7:1 molar ratio of salt to polymer repeat unit, i.e. $(PEO)_7 LiBF_4$.

2. Experimental details

Fluka extrapure product LiBF$_4$ and BDH product PEO of 4 000 000 M.W. were used as received. The $(PEO)_7 LiBF_4$ complex was prepared from acetonitrile solutions by the casting procedure commonly used in our laboratory for the preparation of PEO-based complexes [8]. After evaporation of the solvent, the complex was kept at 40° C under vacuum for 3 days and then further dried by storing it for 2 days in a controlled environment (less than 10 p.p.m. water) dry-box. The final product was a colourless film of about 50 μm thickness.

The electrochemical characteristics were determined by sandwiching a few layers of the polymer complex between two metal electrodes. The cells so formed were then sealed in a glass envelope, removed from the dry-box and placed in an oil-bath thermostat for temperature control.

The nature of the metal electrodes used in the cells varied according to the specific measurement required. The total conductivity was obtained by using two blocking stainless steel (SS) electrodes and determining the complex impedance response, using a Solartron Mod. 1250 frequency response analyser. The electronic conductivity was evaluated using a lithium and stainless steel electrode and measuring the steady-state current after a d.c. voltage pulse, still under blocking polarities, this measurement being run and controlled by a Solartron electrochemical interface (Mod. 1286).

The lithium transport number was evaluated using the electrochemical method proposed by Bruce and Vincent [9], in a cell with two lithium electrodes. The kinetics and the passivation of the lithium electrode were estimated with cells again based on two lithium electrodes. The characteristics of the lithium plating–stripping process were investigated using cells with a nickel cathode and lithium anode.

The differential scanning calorimetry (DSC) analysis was performed using a Perkin Elmer DSC-2 instrument. The samples of polymer complexes sealed in aluminium pans were scanned between 300 and 500 K with a programmed rate of 10 deg min^{-1}. As purge gas dry N$_2$ (99.99%) was used.

3. Results and discussion

Figure 1 shows the complex impedance spectrum at 80° C of the $(PEO)_7 LiBF_4$ complex in a cell with two blocking SS electrodes. Using the equivalent circuit commonly proposed [10] for the interpretation of the spectra of polymer complexes under blocking conditions, the intercept with the real axis in Fig. 1 gives the bulk resistance, R_b, of the $(PEO)_7 LiBF_4$ compound. By repeating the measurement with a heating–cooling cycling, the temperature dependence of the conductivity is obtained.

Figure 2 shows the results. It may be noticed that the temperature dependence of the conductivity in the heating scan is that typically expected for lithium, PEO-based polymeric electrolytes. At about 60° C there is a jump in conductivity corresponding to the crystalline to amorphous change of the complex [1]. Beyond this temperature the conductivity increases more gradually (again typical of the amorphous PEO-based systems), to reach at 125° C about 0.001 Ω^{-1} cm^{-1}, i.e. a value comparable with, even if not higher than, that offered at the same temperature by other and more popular PEO complexes, for instance those based on LiClO$_4$ or LiCF$_3$SO$_3$ [2].
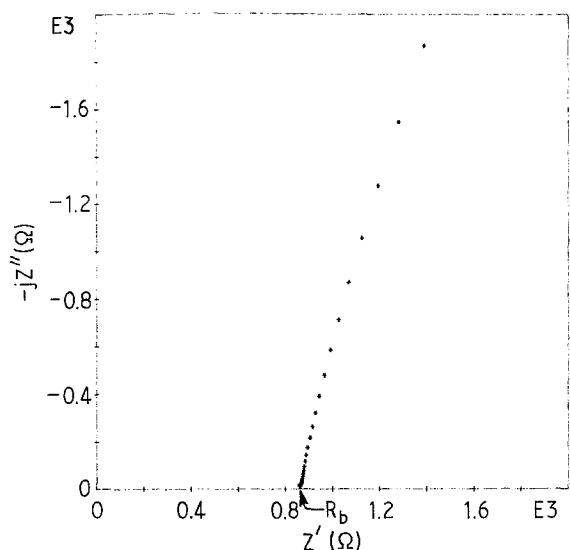
Fig. 1. Complex impedance plot of the SS/(PEO)$_7$LiBF$_4$/SS cell at 80°C.

Fig. 3. Differential scanning calorimetry heating and cooling traces of the (PEO)$_7$LiBF$_4$ complex. Scan rate: 10 deg min^{-1}.

However, Fig. 2 reveals another interesting aspect of the (PEO)$_7$LiBF$_4$ complex under study: the conductivity values obtained in the cooling scan are apparently higher than the corresponding ones obtained in the preceding heating scan. Such a hysteresis between heating and cooling scans has often been noted in polymer electrolytes and indicates slow kinetics in the re-equilibriation of phases of the (PEO)$_7$LiBF$_4$ complex.

This seems to be confirmed by the DSC traces of the complex shown in Fig. 3. In the heating scan a large endothermic peak is revealed at about 60°C, i.e. melting of PEO to which the jump in conductivity discussed in Fig. 2 corresponds.

At 115°C another endothermic peak, probably related to the fusion of the complex, appears in the heating scan. However, no peaks are observed in the following cooling trace, this confirming the slow re-equilibriation effect already revealed by the conductivity behaviour.

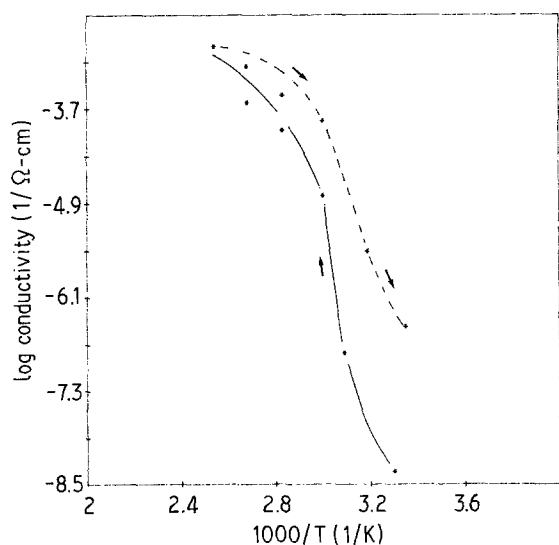In this work, attention was mainly focused on

Fig. 2. Conductivity vs temperature of the (PEO)$_7$LiBF$_4$ complex heating cycle (——); cooling cycle (– – –). Stainless steel electrodes.
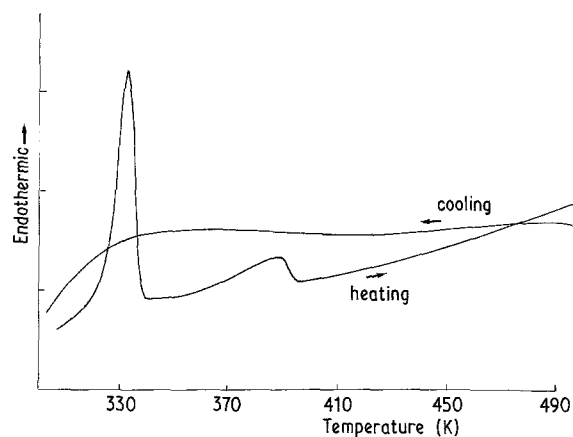
the evaluation of the practical application of the (PEO)$_7$LiBF$_4$ complex as a polymeric electrolyte. The electronic contribution to the total conductivity was determined by applying a d.c. pulse to a SS/(PEO)$_7$LiBF$_4$/SS blocking electrode cell and following the current to its steady-state regime. The values obtained are several orders of magnitude lower than those of Fig. 2 and this clearly indicates that the (PEO)$_7$LiBF$_4$ complex has a conductivity mainly ionic in character and thus that it may be considered as a true polymeric electrolyte.

The lithium transport number t_{Li}^+ was evaluated using the method proposed by Bruce and Vincent [9]. The method is based on a combination of a.c. and d.c. polarizations on a symmetrical cell using two lithium electrodes. By a.c. impedance analysis the initial resistance R_0 of the cell is determined. Then, by applying a small d.c. bias, ΔV, the initial current, I_0, flowing through the cell is measured and monitored with time until it reaches a steady value I_s. Effectively, under a d.c. polarization, a fall in current is expected in a symmetrical cell using a polymer electrolyte because of a combination of factors, which include growth at the electrodes of passivation layers and the establishment of a concentration gradient. Once steady-state conditions are reached, the resistance of the cell, R_s, is again determined by a.c. impedance, and, according to the analysis of Bruce and Vincent [9], the transport number, t^+, is given by:

$$t^+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \qquad (1)$$

In the case under study, the analysis has been performed in a Li/(PEO)$_7$LiBF$_4$/Li cell at 75°C. Figure 4A shows the complex impedance response of the cell to an a.c. signal of 10 mV peak-to-peak. The value of R_0 is here given by the second high-frequency arc and amounts to 5900 Ω. A small d.c. polarization of 30 mV was applied to the cell and the resulting current was monitored with time until stabilization (steady state) was reached. From the current–time behaviour, the values of I_0 and I_s were determined to be 1.8 μA and 0.93 μA, respectively. Figure 4B shows
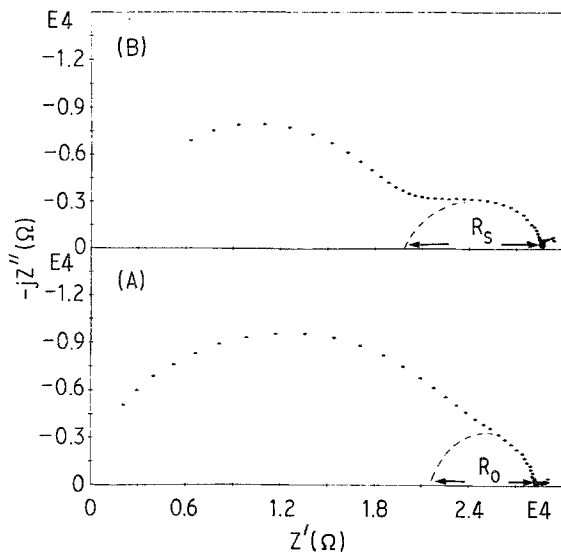
Fig. 4. Complex impedance plot of the Li/(PEO)₇LiBF₄/Li cell at 75°C before (A) and after d.c. polarization (B). The plot (B) was obtained after a steady-state condition was reached. Electrolyte thickness: 1.5 mm.

the complex impedance response under steady state conditions: the high-frequency arc has expanded, giving an R_s value of 8210 Ω.

Using the quoted values in Equation 1, we obtain for the (PEO)₇LiBF₄ electrolyte a value of t_{Li}^+ of about 0.8 at 75°C.

This is an interesting result which indicates that in PEO–LiBF₄ polymer electrolytes lithium is the major ionic carrier. However, one has to point out that transport number measurements in polymer electrolytes are very difficult [11] and that the resulting values have to be taken with caution. It is safe to state here that the (PEO)₇LiBF₄ complex is a good lithium polymer electrolyte which, due to this characteristic, may find important practical applications.

In this respect, it has appeared to us of importance to determine the kinetics of the lithium electrode in (PEO)₇LiBF₄-based cells.

As already pointed out, Fig. 4A, shows the complex impedance response of a (PEO)₇LiBF₄ cell using two lithium, non-blocking electrodes. Two semicircles may be observed in the complex plane. The high-frequency semicircle may be associated to the electrode/electrolyte interface and the intercept with the real axis furnishes the value of the related charge-transfer resistance, R_{ct}.

By repeating the impedance analysis at various temperatures, it is possible to investigate the thermal properties of the (PEO)₇LiBF₄ interface. In the range of stability of the crystalline phase, the charge transfer resistance is very low, i.e. of the order of 20 kΩ. After the complex phase changes, the interface conditions improve consistently and the charge transfer resistance decays by several orders of magnitude, assuming at 373 K the value of 125 Ω, with a corresponding exchange current density of approximately 0.6 mA cm⁻².

Such a value confirms the interest of the (PEO)₇ LiBF₄ as polymeric electrolyte for the devel-

opment of lithium-based electrochemical devices. However, for this type of application, especially if directed to rechargeable batteries, it is also of importance to evaluate the cyclability and the stability of the lithium electrode in the given electrolyte medium.

The cyclability has been examined by studying the characteristics of the plating and stripping process on nickel, i.e. a metallic substrate of common use in lithium battery technology. Figure 5 shows the cyclic voltammetry of the process at 80°C. On the first cathodic scan the voltage required to deposit lithium metal on the nickel surface is some 50 mV negative, probably because of electrocrystallization overvoltage (mismatch of lithium and nickel lattice spacings). Once a monolayer has been formed, however, further plating can occur at any potential below 0 V (vs Li) and the stripping peak appears in the anodic scan. The cyclability is good and the recovery of lithium high.

The stability of the lithium electrode in the PEO–LiBF₄ polymer complex, has been evaluated by a.c. complex impedance analysis. Figure 6 shows the evolution of the complex impedance response of a Li/(PEO)₇LiBF₄/Li cell at progressively longer times of storage at 81°C. It may be clearly seen that the high frequency semicircle, and thus the resistance of the lithium interface, increases with storage time. This in turn reveals that passivation of the lithium electrode takes place at the interface with the growth of a non-conductive layer on the electrode surface, possibly as the result of a decomposition reaction of the electrolyte.
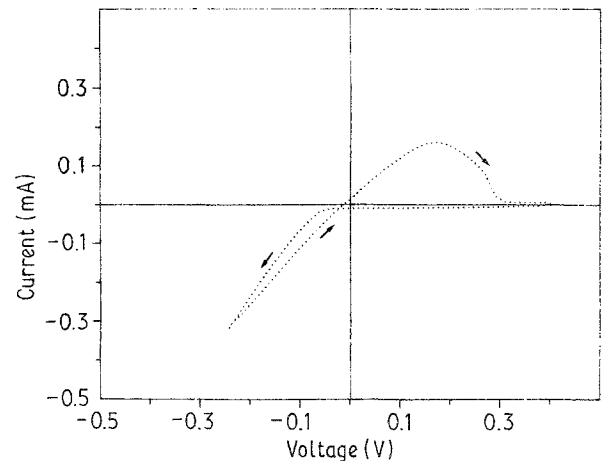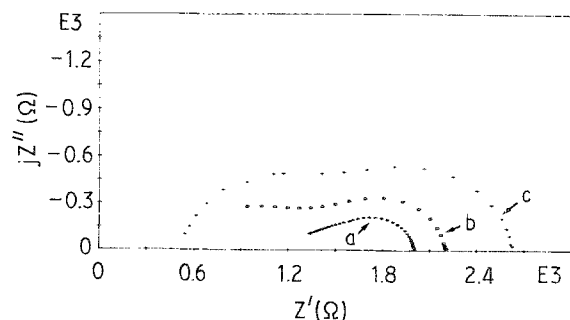

Fig. 5. Cyclic voltammetry of the lithium plating–stripping process on a nickel support at 80°C from a cell using the (PEO)₇LiBF₄ electrolyte. Sweeping rate: 20 mV s⁻¹. Electrode surface: 1.13 cm².

Fig. 6. Complex impedance plots of the Li/(PEO)₇LiBF₄/Li cell upon time of storage at 81°C. (a) 1 h; (b) 6 h; (c) 25 h.

It is difficult to evaluate what influence this passivation effect might have on the behaviour of a rechargeable lithium battery. By comparison with what is generally observed in batteries using lithium organic electrolytes [11], one would expect that the passivation could seriously limit the cycling life of the lithium electrode.

However, passivation effects similar to those described here for the $Li/(PEO)_7LiBF_4$ interface have been observed by Fauteux [12] and by us [13] also for interfaces using the $(PEO)-LiClO_4$ and the $PEO-LiCF_3SO_3$ complexes. These polymeric electrolytes are currently used for the development of rechargeable lithium cells which are reported as capable of sustaining several hundred cycles [3, 4]. Therefore, one has to conclude that Li passivation effects are less crucial in polymeric batteries than in organic electrolyte batteries, probably because the former use configurations with a much larger electrode surface area. Under these circumstances also the $(PEO)_7LiBF_4$ complex described here may find a competitive place among the family of lithium polymer electrolytes of interest for rechargeable lithium batteries, especially considering the comparatively higher values of conductivity, of lithium transport number and Li exchange current density in the vicinities of $100°C$.

To test this assumption, a battery of the type:

$$Li/(PEO)_7LiBF_4/Li_{1+x}V_3O_8 \qquad (2)$$
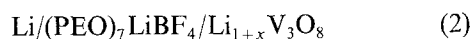
has been assembled. The vanadium bronze $Li_{1+x}V_3O_8$ is an intercalation compound with excellent properties as positive electrode in lithium cells [14]. This material also shows a very promising behaviour in lithium, polymer electrolyte batteries. In fact, good cycling performance has been obtained with cells using the $Li/Li_{1+x}V_3O_8$ couple in polymer complexes of the $(PEO)_8LiClO_4$ and $(PEO)_9LiCF_3SO_3$ types [15].

This promising behaviour is also confirmed in the case under study here. In fact, cell (2) has an open-circuit voltage of $3.6V$ (at $80°C$) and shows the charge–discharge cycling performance illustrated in Fig. 7.

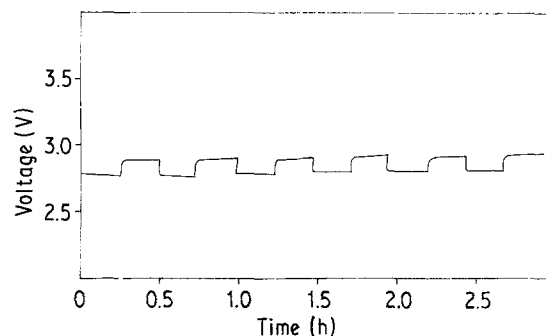Fig. 7. Shallow charge–discharge cycles of the $Li/(PEO)_7LiBF_4/Li_{1+x}V_3O_8$ cell at $100°C$. Charge–discharge capacity: 0.025 mAh.

Acknowledgements

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