

## THE LITHIUM POLYMER ELECTROLYTE BATTERY IV. USE OF COMPOSITE ELECTROLYTES

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### Summary

The properties of composite polymer electrolytes formed by adding inert ceramic fillers to the standard poly(ethylene oxide)-lithium salt complexes are illustrated in terms of ionic conductivity and of mechanical properties. The use of these electrolytes in rechargeable lithium batteries is also discussed and evaluated.

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### Introduction

Complexes between high-molecular weight poly(ethylene oxide) (PEO) and lithium salts (*e.g.*,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiBF}_4$ ) are suitable for the realization of high-energy, rechargeable lithium batteries [1]. These batteries operate at temperatures of the order of 80 - 100 °C to assure a reasonably high electrolyte conductivity. In fact, fast ion transport is necessarily associated with an amorphous state of the polymer complexes. Under these conditions, the complexes behave like highly viscous liquids and thus generally have poor mechanical properties. Direct use of the polymers may then result in problems commonly met with in conventional liquid electrolyte systems, such as passivation of electrodes and leakage.

It is therefore desirable to stabilize the lithium electrode interface by the use of electrolytes having improved high-temperature morphological characteristics. We have tried to realize this condition by using composite electrolytes formed by the addition of inert fillers (such as small grain size  $\beta$ "- $\text{Al}_2\text{O}_3$ ) to "conventional" polymer complexes (such as  $(\text{PEO})_8\text{LiClO}_4$ ). These composite electrolytes are chemically similar to the pure complexes but have highly improved mechanical properties [2]. In fact, the fillers provide a supporting matrix for the conductive amorphous polymer so that

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the composite retains, even at high temperature, an overall solid structure still maintaining at microscopic level the liquid-like configuration necessary to assure fast ionic mobility. Furthermore, the conductivities of the composite electrolytes are comparable with those of the pure electrolytes, provided that the particle size of the filler is sufficiently small (*i.e.*, lower than 5  $\mu\text{m}$ ).

The validity of this approach has been demonstrated by various authors [3 - 6], and in this work we report on an investigation of the properties of lithium ion, conducting composite electrolytes (formed by the addition of  $\beta''$ -alumina to the  $(\text{PEO})_8\text{LiClO}_4$  complex) and of their use in rechargeable lithium batteries.

## Experimental

High molecular weight ( $M_w = 4\,000\,000$ ) poly(ethylene oxide), PEO, a pure BDH product, and lithium perchlorate ( $\text{LiClO}_4$ ), a Fluka reagent grade product, were used as received. The  $\beta''\text{-Al}_2\text{O}_3$  powders were produced according to a sol-gel procedure described in detail elsewhere [7]. Basically, the powders were obtained by water extraction, using 2-ethyl-1-hexanol, from the sol drops in order to obtain the spherical particles typical of the sol-gel process. After milling for 3 h, powders having a mean particle size of 13  $\mu\text{m}$  were obtained. To separate the various granulometric fractions, a sedimentation method, carried out in a suitable viscous liquid, was utilized. The mean particle size of the powders so obtained was less than 5  $\mu\text{m}$ .

Appropriate weights of  $\text{LiClO}_4$  and PEO, to give an O:Li ratio of 8:1 in the complex, were dissolved in HPCL grade acetonitrile (Aldrich, glass distilled, filtered through 0.5  $\mu\text{m}$  filters, water content less than 0.003%). The solutions were then stirred for 20 h at room temperature in a stoppered flask. A known amount of  $\beta''\text{-Al}_2\text{O}_3$  powder was added and the solution stirred continuously by a high-intensity ultrasonic finger directly immersed in the solution in order to separate the particles and facilitate solution of the PEO. When homogenization of the mixture had occurred, it was cast onto flat poly(tetrafluoroethylene) sheet and covered to allow slow evaporation of the acetonitrile. By this procedure homogeneous polymer films, 25 - 50  $\mu\text{m}$  thick, with no optical evidence of powder agglomeration, were obtained. All further manipulation of these films was carried out in an argon-filled glove-box, having less than 10 ppm water content.

The purity of the electrolyte films was controlled by differential scanning calorimetry (DSC) measurements carried out by a Mettler TA 3000 system over a temperature range of 30 - 140  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C min}^{-1}$  using hermetically sealed samples. Only one endothermic peak at approximately 69  $^\circ\text{C}$  is detectable in the heating cycle (Fig. 1). This peak, corresponding to the crystalline-to-amorphous phase transition, is typical of PEO complexes [8], and thus the trace of Fig. 1 confirms the absence of any chemical reaction between the ceramic powders and the polymer complex.

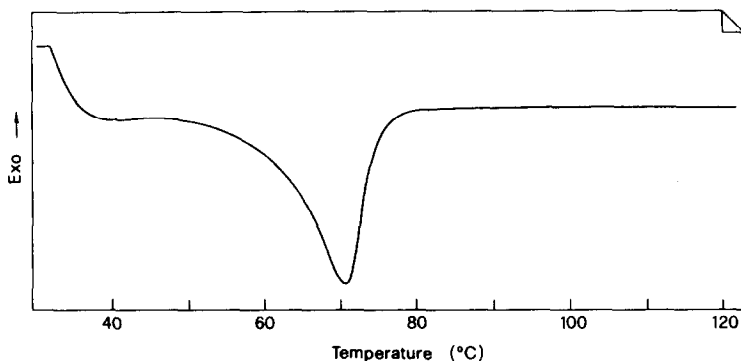


Fig. 1. DSC trace for the  $(\text{PEO})_8\text{LiClO}_4 \cdot 10 \text{ wt.}\% \beta''\text{-Al}_2\text{O}_3$  composite electrolyte.

The electrical properties of the electrolyte films were characterized by a.c. impedance spectroscopy over a frequency range of 0.1 - 65 kHz, using a Solartron 1250 frequency analyser and a Solartron 1286 electrochemical interface, both coupled to an HP-Vectra computer.

A best fitting of the experimental impedance data, performed by a non-linear least-squares analysis program, with a modified Levenberg-Marquardt algorithm (we adapted to Boukamp [9] EQIVCT original code), was used to obtain the equivalent circuit parameter values of the samples. Two plane, stainless steel, parallel, metallographic-grade polished electrodes, with a surface area of  $1.54 \text{ cm}^2$ , were used. The cells were kept under a constant mechanical pressure. The results of both the first and the second temperature rises were recorded.

For the battery test, a composite cathode based on a titanium sulfide ( $\text{TiS}_2$ ) intercalation compound (kindly provided by Dr K. Abraham of EIC, Mass. U.S.A.) was chosen. This compound was mixed with acetylene black (20 wt.%) and the  $(\text{PEO})_8\text{LiClO}_4$  standard electrolyte (40 wt.%) and cast from purified acetonitrile to obtain a film having a plastic nature and a thickness similar to that of the polymer electrolyte films [10].

A two-electrode cell of the spring-loaded, button type was used for the cycling test. This cell was prepared by contacting a lithium disk (about 1 mm thick), polymer electrolyte disks (total thickness about  $75 \mu\text{m}$ ), the positive electrode film (about  $75 \mu\text{m}$  thick), and a nickel current collector. The surface area of the cell was  $1 \text{ cm}^2$ .

The cells were assembled in the dry box and then kept at constant temperature ( $\pm 0.5 \text{ }^\circ\text{C}$ ) by a Buchi model TO-51 oven. The cells were automatically cycled by a voltage-controlled timer.

## Results and discussion

While extensive study has been dedicated to the overall behaviour of polymer electrolyte, lithium batteries, relatively few investigations have been

directed to the cyclability of single electrodes and, in particular, to the cyclability of the lithium electrode.

Figure 2 shows the evolution of the a.c. complex impedance response of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4/\text{Li}$  cell stored at  $80^\circ\text{C}$ . It will be clearly seen that the low-frequency semicircle increases with storage time. By circuit analysis [11, 12] this semicircle may be associated with the electrode interface, and thus Fig. 2 reveals that passivation of lithium takes place, with a growth at the interface of a non-conductive layer, possibly as the result of a decomposition reaction of the "conventional" polymer electrolyte [13].

It is well documented [14] that passivation of lithium, which is common in liquid, organic electrolytes, results in a progressive loss of cycling efficiency due to irregular, dendritic-type deposition of lithium upon cycling. It is possible that a similar effect may also take place in polymer electrolytes, especially when operating at high temperature. Indeed, evidence of dendrite formation has been observed during prolonged cycling tests of lithium batteries using the "conventional"  $(\text{PEO})_8\text{LiClO}_4$  polymer electrolyte [15]. Therefore, it appears desirable to stabilize the lithium electrode interface by the use of polymer electrolytes having improved high-temperature morphological characteristics. We have attempted to attain this condition using composite electrolytes formed by the addition of an inert filler, *i.e.*, small grain size  $\beta''\text{-Al}_2\text{O}_3$ , to a conventional polymer complex, *i.e.*,  $(\text{PEO})_8\text{LiClO}_4$ .

Generally, composite electrolytes of this kind have chemical properties similar to those of the pure complexes (see Fig. 1) combined with greatly improved mechanical properties [2, 6]. Furthermore, the conductivity of the composite electrolytes is comparable with [6], if not even higher [5] than, that of pure electrolytes, provided that the particle size of the filler is sufficiently small (*i.e.*, lower than  $5\ \mu\text{m}$ ). This has been verified in the case here examined; indeed, Fig. 3 shows that the composite electrolyte formed by the addition of 10 wt.% of  $\beta''\text{-Al}_2\text{O}_3$  to the  $(\text{PEO})_8\text{LiClO}_4$  complex has a conductivity of the same order as that of the complex itself. Figure 4 shows the evolution of the a.c. impedance response of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4\text{-}10\ \text{wt.}\% \beta''\text{-Al}_2\text{O}_3/\text{Li}$  cell stored at  $80^\circ\text{C}$ . It may be noticed that the interface resistance, determined by the low frequency intercept,

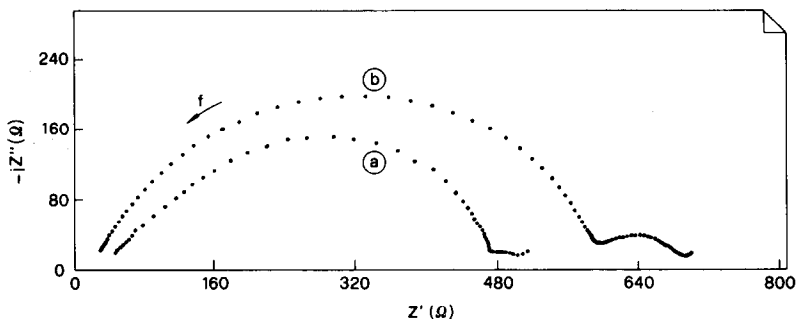


Fig. 2. Evolution of the a.c. complex impedance response of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4/\text{Li}$  cell at  $80^\circ\text{C}$ . (a) Fresh; (b) after 8 days storage. Frequency range: 0.02 Hz - 65 kHz.

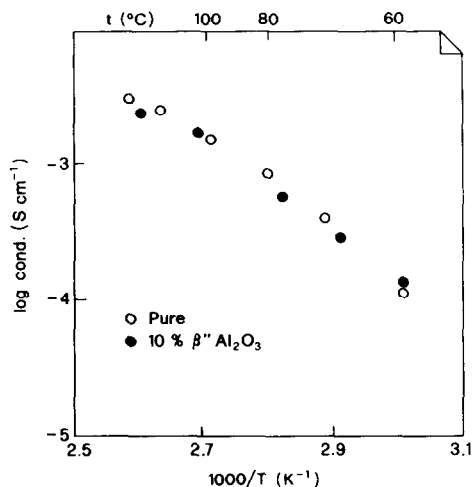


Fig. 3. Conductivity of the pure  $(\text{PEO})_8\text{LiClO}_4$  and of the composite  $(\text{PEO})_8\text{LiClO}_4 \cdot 10 \text{ wt.}\% \beta''\text{-Al}_2\text{O}_3$  electrolyte at temperatures above the crystalline-to-amorphous transition.

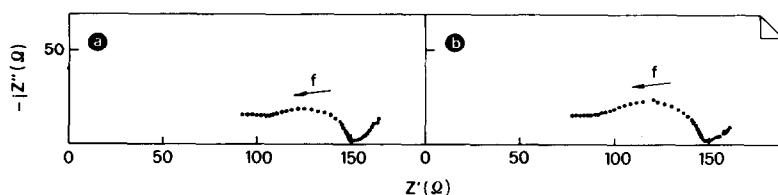


Fig. 4. Evolution of the a.c. impedance response of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4 \cdot 10 \text{ wt.}\% \beta''\text{-Al}_2\text{O}_3/\text{Li}$  cell at  $80^\circ\text{C}$ . (a) Fresh; (b) after 8 days storage. Frequency range: 0.02 Hz - 65 kHz.

does not significantly change upon storage. This indicates that the passivation of lithium is indeed much lower when the metal is in contact with the hard, composite electrolyte, than it is when in contact with the soft, pure polymer complex (compare Fig. 2).

Such an improvement in interfacial conditions should result in enhanced cycling behaviour in rechargeable batteries. We have investigated this aspect by assembling a cell formed by a lithium foil, a film of the composite electrolyte, and a film of a cathodic mixture consisting of titanium sulphide (the active intercalation electrode), acetylene black (to improve the electronic conductivity of the entire cathodic mass), and polymer electrolyte (to provide a plastic configuration to the cathodic film).

The cell has been cycled at  $100^\circ\text{C}$  and under various conditions. Figure 5 illustrates the results. The second cycle, run at a  $C/5$  rate, shows well-defined plateaux typical of the  $\text{Li}/\text{TiS}_2$  couple and a good cycling efficiency (92%). At cycle 75, the plateaux are still well defined, with charge and discharge overvoltages similar to those observed in the first cycles. How-

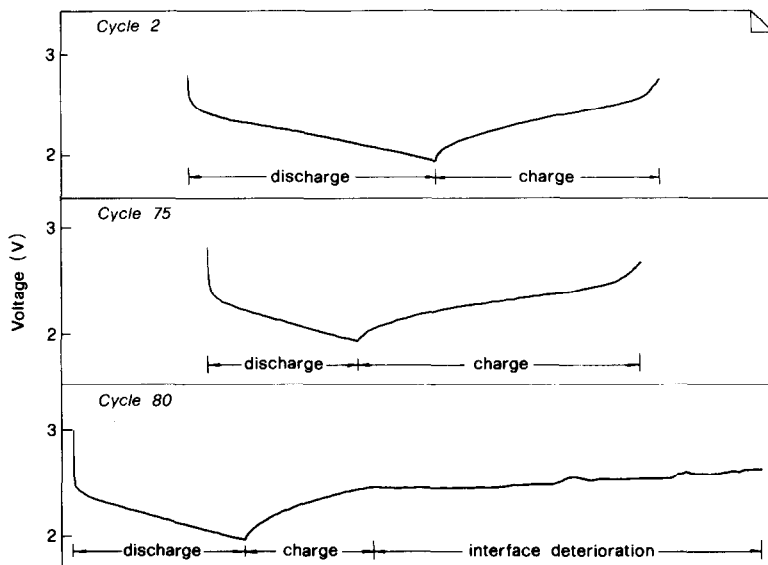


Fig. 5. Cycling voltage profiles of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4 \cdot 10 \text{ wt.}\% \beta''\text{-Al}_2\text{O}_3/\text{TiS}_2$  battery at  $100^\circ\text{C}$  and at  $C/5$  rates.

ever, the cycling efficiency has decayed to 70%. This latter effect is probably associated with the cathodic side of the cell and related to the inefficiency of the Li insertion process into, and out of, the  $\text{TiS}_2$  structure. Similar effects are generally observed upon cycling lithium polymer electrolyte batteries using intercalation cathodes [1, 6]. The point of interest here is that the shapes of the discharge and the charge curves remain virtually unchanged, this indicating that the integrity of the interfaces has been preserved upon cycling, as expected when using the composite hard electrolyte. Only occasionally has some erratic behaviour in the charging voltage been noticed. Such behaviour, which on the other hand is quite frequent in cycling batteries using a "conventional" soft electrolyte [15], may be associated with the growth of lithium microdendrites upon charging.

In the case under study here, the normal voltage profiles could be easily restored just by decreasing the charging rate (for instance, passing from the  $C/5$  to the  $C/10$  rate). Under these conditions the battery could be recharged effectively for many cycles with reasonable efficiency and appreciable capacity recovery (Fig. 6). The decay in capacity upon cycling is associated with the diffusion limits of the lithium intercalation process that results in the already mentioned progressive inefficiency of the intercalation reaction. However, even after long cycling, high utilization may still be achieved by decreasing the cycling rates and by expanding the discharge voltage limits.

This type of behaviour cannot be achieved with batteries using pure PEO-based polymer electrolytes, at least with the samples examined under comparable conditions in our laboratory.

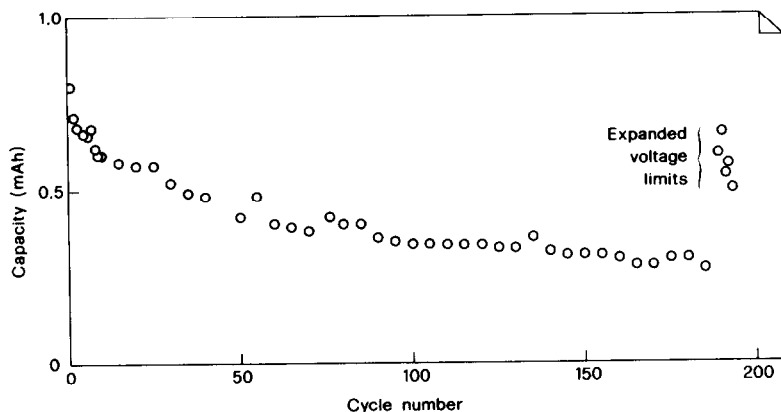


Fig. 6. Cycling behaviour of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4 \cdot 10 \text{ wt.}\% \beta''\text{-Al}_2\text{O}_3/\text{TiS}_2$  button-type cell at  $100^\circ\text{C}$  and  $C/5$  (cycles 0 - 70) and  $C/10$  (cycles 71 - 190) discharge rate. Cycling voltage limits 1.9 - 2.7 V (cycles 0 - 185) and 1.5 - 2.7 V (last 5 cycles).

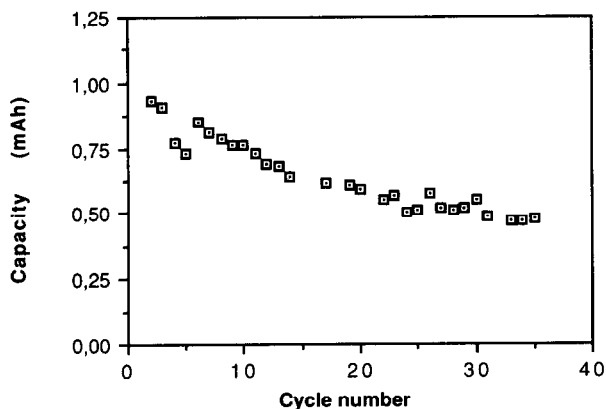


Fig. 7. Cycling behaviour of an  $\text{Li}/(\text{PEO})_8\text{LiClO}_4/\text{TiS}_2$  button-type cell at  $100^\circ\text{C}$  and at  $C/5$  discharge rate. Cycling voltage limits 1.9 - 2.7 V.

Figure 7 illustrates the cycling response of a battery of the type  $\text{Li}/(\text{PEO})_8\text{LiClO}_4/\text{TiS}_2$ . The battery failed after 35 cycles due to the poor charging recovery, this being typically associated with dendrite shorting upon cycling. Therefore, and in conclusion, the results presented here, tend to confirm that the composite electrolyte may be more profitably used than the pure PEO complexes for the development of long-life, rechargeable lithium batteries.

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## References

- 1 J. R. MacCallum and C. A. Vincent (eds.), *Polymer Electrolyte Review I*, Elsevier Applied Science, London, 1987.
- 2 B. Scrosati, *J. Electrochem. Soc.*, **136** (1989) 2774.
- 3 J. E. Weston and B. C. H. Steele, *Solid State Ionics*, **7** (1982) 75.
- 4 Chen Liquan, in B. V. R. Chowdari and S. Radhakrishna (eds.), *Materials for Solid State Batteries*, World Scientific Publishing Co., Singapore, 1986, p. 69.
- 5 W. Wiczołek, K. Such, J. Plocharski and J. Przyłuski, *Proc. 2nd Int. Symp. Polymer Electrolytes (ISPE 2)*, Siena, Italy, 1989, Elsevier, London, 1990, p. 339.
- 6 F. Croce, F. Bonino, S. Panero and B. Scrosati, *Philos. Mag. B*, **59** (1989) 161.
- 7 M. Carewska, F. Croce, F. Deptula, A. Di Bartolomeo and C. Majani, in P. Vincenzini (ed.), *High Technology Ceramics*, Elsevier, Amsterdam, 1987, p. 1901.
- 8 D. Fauteux, M. D. Lupien and C. D. Robitaille, *J. Electrochem. Soc.*, **134** (1987) 2761.
- 9 B. A. Boukamp, *Solid State Ionics*, **20** (1986) 31.
- 10 A. Selvaggi, F. Croce and B. Scrosati, *J. Power Sources*, **32** (1990) 389.
- 11 D. Fauteux, *Solid State Ionics*, **17** (1985) 133.
- 12 S. Morzilli, F. Bonino and B. Scrosati, *Electrochim. Acta*, **32** (1987) 961.
- 13 D. Fauteux, *J. Electrochem. Soc.*, **135** (1988) 2231.
- 14 K. M. Abraham and S. B. Brummer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, p. 371.
- 15 B. Scrosati, A. Selvaggi, F. Croce and Wang Gang, *J. Power Sources*, **24** (1988) 287.