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Polymer Electrolytes

The Route Towards Solid Polymer Electrolytes with Stable Electrochemical Performances Upon Long Term Storage

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SUMMARY

The room temperature conductivity of lithium salts dissolved in polyethylene oxide, proposed as polymer electrolytes, is shown to decrease drastically upon storage. The crystallization process, which is responsible for that ageing, can be blocked, if two further components are added : an elastomer copolymer butadiene-acrylonitrile and a macromer of polyoxyethylene. In addition, a crosslinking process must be carried out.

INTRODUCTION

Since the discovery by Armand [1] that solid materials obtained by dissolving alkali metal salts in polyalkylene oxide can be used as solid electrolytes in batteries, an increasing interest has been devoted to the study of these systems, especially those based on polyethylene oxide [2-10]. It seems now accepted that the ion transport involves the amorphous phase rather than the crystalline ones [4, 5, 9, 11], a WLF law being obeyed when the temperature is varied [12]. Recent studies show the interest of more amorphous polymers (aliphatic polyesters [13]), of strongly acidic counterions [14], and of polymers with short polyoxyethylene branches [14-17]. Nothing has been published up to now on the behavior of these systems upon ageing, when storing the electrolyte in contact with lithium. The present paper shows first that the ionic "conductivity" at room temperature decreases in general drastically upon storage. It also shows how it may be maintained using a complex composite material [17]. An extended study of the electrochemical properties of the high performance systems obtained will be published in the near future [20, 21].

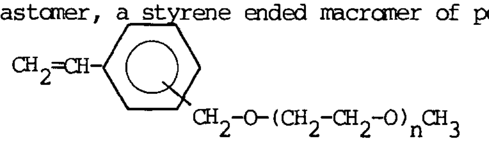
RESULTS AND DISCUSSION

The components of the solid electrolyte are first dissolved in dry acetonitrile ; the solvent is removed from a teflon flat container, under an argon stream, to give a membrane that may be stored in a glove box under argon. The solid electrolyte membrane is placed between a lithium anode and a composite cathode of MnO_2 impregnated with a solution of $LiClO_4$ in polyethylene oxide (PEO) of 0.9 10^6 molecular weight, pressed under 2 tons in a closed button and treated 1 hour at 100°C. The solid state battery Li/ES/MnO_2 is then stored at 35°C.

After ageing, a set of galvanoplastic pulses (5 ms/sec) is applied and the intensity of the current delivered under a 1.5 volt tension at the end of the pulse. The experiment is carried out at various storage time and the result is a plot of that current versus the storage time (fig. 1-5). As shown in figure 1, the conductivity of the $LiClO_4$, PEO system drastically decreases after a few hours of storage. DSC experiments (fig. 6) for the same system show that this decrease is parallel to a crystallization process that may involve the polyethylene oxide itself (peak at 62°C) ; the peak at 71°C being probably associated with a crystal phase including the lithium cation in a PEO helix. The replacement of $LiClO_4$ by $LiCF_3SO_3$ in the electrolyte also leads to a less drastic decrease in the conductivity (fig. 2) ; the corresponding membrane is less sticky and the DSC shows only one peak at 56°C after 100 hours.

As shown in figure 3, an important improvement (related with the ageing process) is obtained upon introduction of a limited amount, i.e. 3.5 % of an elastomer butadiene-acrylonitrile (18 %) copolymer.

But the real breakthrough is obtained [17] when, in addition to the elastomer, a styrene ended macromer of polyethylene oxide [18]



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is added in partial replacement of polyethylene oxide, the ethylene oxide unit/Li^+ weight ratio being kept constant (8 with $LiClO_4$ or 11.8 with $LiCF_3SO_3$). In this case, provided a radical treatment is applied on amorphous material, very good results can be obtained. The treatment that may be either thermal or radiative (Xray) involves both the polymerization of the macromer and the crosslinking of the elastomer.

The macromer reactivity was shown to be very similar to that of styrene [18] and does not seem to be affected by the length of the PEO oligomer chain attached to it. The crosslinking process may occur owing to the transfer process involving a CH_2 group vicinal to an internal double bond of the 1-4 butadiene unit, but is also probably done via copolymerization of the macromer with the vinyl double bond of the 1-2 butadiene ; such a process causes the macromer to be grafted onto the elastomer backbone, which, in turn, becomes more compatible to the polyethylene oxide. This grafted elastomer induces amorphisation of the medium, so that the conductivity may be increased ; in addition, the crosslinking process tends to fix the state of the matter, so that the crystallization process which relates to the ageing is inhibited. During the polymerization, the benzylic nature of the chain end of the macromer induces a rather high activity as a transfer agent, thus causing some extra crosslinking. As shown by figure 4, the replacement of the macromer with a styrenic chain end by a corresponding oligomer with a saturated benzylic chain end leads to a good, although always inferior electrochemical behaviour. The best results are shown in figure 5, using both $LiCF_3SO_3$ and rather high amount (between 20

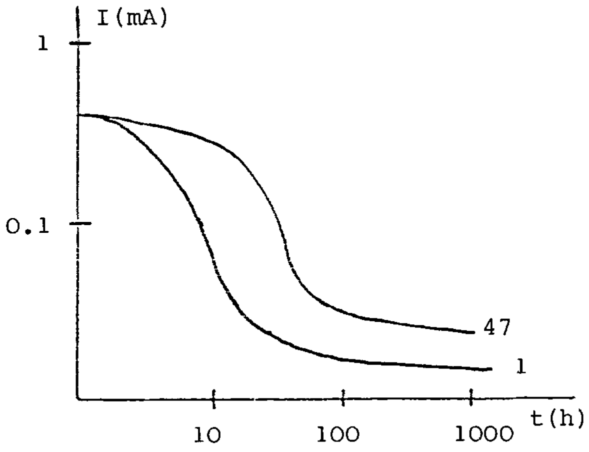

Figure 1 - Delivered current (mA) versus storage time for electrolyte of $LiClO_4$ in polyethylene oxide of molecular weight 4.10^6 (run 1) or in a mixture of polyethylene oxide of molecular weight 9.10^5 (90%) and 10^5 (10%) (run 47)

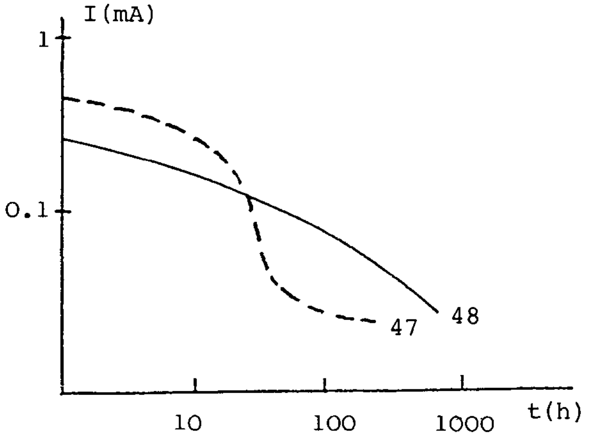

Figure 2 - Delivered current (mA) versus storage time for electrolyte of $LiClO_4$ (run 47) or $LiCF_3SO_3$ (run 48) in a mixture of polyethylene oxide of molecular weight 9.10^5 (90 %) and 10^5 (10%)

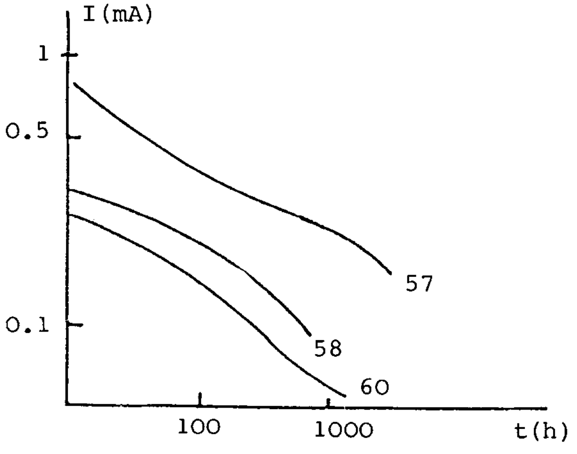

Figure 3 - Electrolytes of $LiCF_3SO_3$ in polyethylene oxide (molecular weight 4.10^6) with, in addition, 3.5 (run 57), 10 (run 58) or 20 % (run 60 of butadiene-acrylonitrile elastomer Perbunan R.

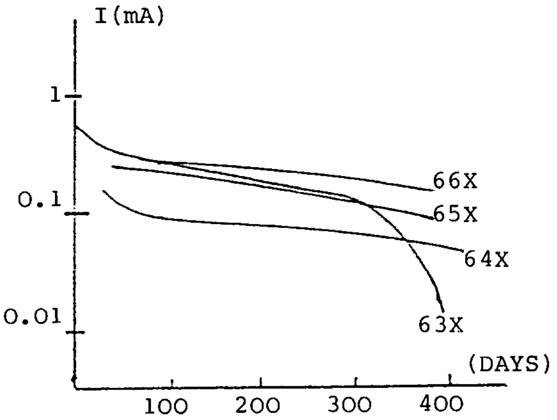

Figure 4 - Long term storage electrochemical performances of composite solid polymer electrolyte including $LiCf_3SO_3$ in polyethylene oxide (molecular weight 9.10^5) 80%, Perbunan (3.5%), and various polyethylene oxide oligomers (20%) used after radiative crosslinking process (X ray 1 hour at 80° C)
run 63 ; benzylic ended oligomer molecular weight 550
run 64 : benzylic ended oligomer molecular weight 1900
run 65 : styrenic ended oligomer molecular weight 1900
run 66 :styrenic ended oligomer molecular weight 5000

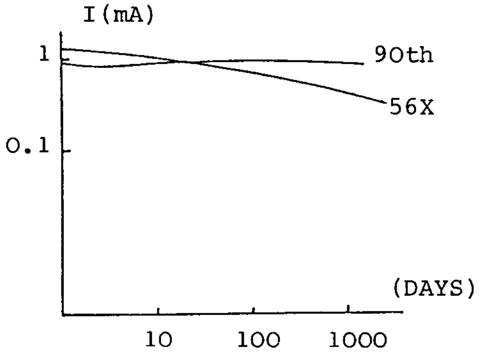

Figure 5 - Very long term storage electrochemical performance of composite solid polymer electrolytes including $LiCF_3SO_3$, polyethylene oxide (molecular weight 9.10^5) (PEO), Perbunan and Styrene ended oligomer (SEO) of molecular weight 550

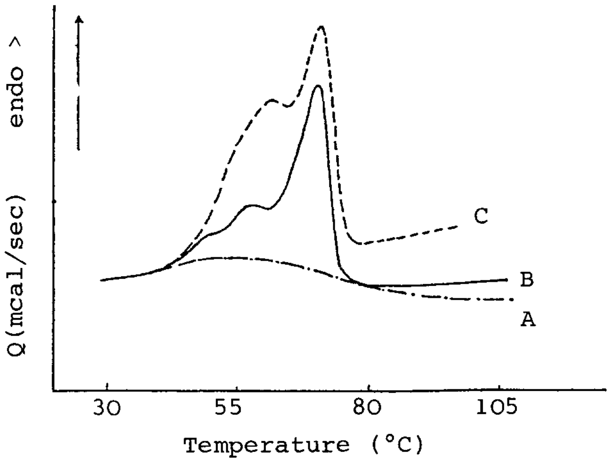

Figure 6 - DSC traces of a $LiClO_4$ polyethylene oxide (molecular weight 9.10^5) membrane after no(A) 24 h(B) or 100 h(C) storage time

and 50 %) of a rather low molecular weight macromer (550) ; they involve a crosslinking process carried out enough time and at a temperature high enough (150°C) so that both complete melting of the crystallites and complete polymerization of the macromer take place. Then a rather high "conductivity" (up to 2.10^{-4} ohm^{-1}/cm) can be reached and kept for a very long storage time (more than 3 years). But we have to underline that, in batteries, the conducitivity is not the only term of dissipation [21] and it is now proved that solid state polymer lithium batteries are limited by 2 major terms :

a) the dynamic space charge originates in the mobility of the anion [21];

b) the blocking interface onto the negative electrode [20].

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REFERENCES

1. M.B. ARMAND, J.M. CHABAGNO and M.J. DUCLOT - Second International Meeting on Solid Electrolytes (extended abstracts) St Andrews (1978) (Scotland)
2. P.V. WRIGHT,Br. Polym. J., 7, 319 (1975)
3. J.M. PARKER, P.V. WRIGHT, C.C. LEE,Polymer, 22 1305 (1981)
4. C.C. LEE, P.V. WRIGHT, Polymer, 23 681 (1982)
5. D.R. PAYNE, P.V. WRIGHT, Polymer, 23 690 (1982)
6. B.L. PAPKE, M.A. RATNER, D.F. SHRIVER, J. Phys. Chem. Sol., 42 493 (1982) and J. Electrochem. Soc., 129 1694 (1982)
7. D.F. SHRIVER, B.L. PAPKE, M.A. RATNER, R. DUPON, T. WRONG and M.BRODWIN, Solid State Ionics, 5 83 (1981)
8. R. DUPON, B.L. PAPKE, M.A. RATNER, D.H. WHITMORE and D.F. SHRIVER, J. Am. Chem. Soc., 104 6247 (1982)
9. J.E. WESTON and B.C.H. STEELE, Solid State Ionics, 7 75 (1982)
10. P.R. SORENSEN and T. JACOBSEN, Electrochim. Acta, 27 1671 (1982)
11. C. BERTHIER, W. GORECKY, M. MINIER, M. ARMAND, M. CHABAGNO and P. RIGAUD, Solid State Ionics, 11 91 (1983) and J. Chim. Phys., 45 739 (1984)
12. A. KILLIS, J.F. LE NEST and H. CHERADAME, Makromol. Chem. Rapid Comm., 1 595 (1980)
13. M. WATANABE, M. RIKUKAWA, K. SANUI, N. OGATA, H. KATO, T. KOBAYASHI and Z. OHTAKI, Macromolecules, 17, 2902, 2908 (1984)
14. D.J. BANNISTER, G.R. DAVIES, J.M. WARD and J.E. Mc YNTYRE, Polymer, 25 1291, 1600 (1984)
15. W.Y. KU and J. SMID, J. Am. Chem. Soc., 106, 3790 (1984) and Makromol.Chem. Rapid. Comm., 5 173 (1984)
16. D.W. XIA and J. SMID, J. Polym. Sci. Polym. Lett. Ed., 22 617 (1984)
17. A. LE MEHAUTE et al. Europ. Patent 0078505
18. A. REVILLON, T. HAMAIDE, Polym. Bull., 6 235 (1982)
19. T. HAMAIDE, A. REVILLON and A. GUYOT, Europ. Polym. J., 20 855 (1984)
20. A. LE MEHAUTE, G. CREPY, G. MARCELLIN, T. HAMAIDE and A. GUYOT (Submitted to Macromolecules)
21. A. LE MEHAUTE, Plenary Conference on "Solid State Electrolyte" Riso meeting (september 1985)

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