

Short communication

Characterization of plasticized solid polymer electrolyte by XRD and AC impedance methods

T. Jose Benedict^a, S. Banumathi^a, A. Veluchamy^{a,*}, R. Gangadharan^a,
A. Zulfiyar Ahmad^b, S. Rajendran^b

^a Central Electrochemical Research Institute, Karaikudi-630006, India

^b Department of Physics, Alagappa University, Karaikudi-630003, India

Received 5 February 1998; accepted 10 February 1998

Abstract

Polymer electrolyte films prepared from poly(ethylene oxide) and lithium hexafluoroarsenate with varying composition of dibutylphthalate, the plasticizing agent, are studied by X-ray diffraction and AC impedance. A film containing 0.09 mol of dibutylphthalate is an optimum electrolyte composition by virtue of its free-standing ability with reasonably high conductivity. A film with this composition exhibits an enhanced amorphous character and a reduced energy barrier to segmental motion which favours lithium-ion conduction through the film. The temperature dependence of the complex film, with and without plasticizer, appears to obey the Arrhenius Law. The activation energy is 0.578 kJ/mol, which is considerably lower than the value of 10 kJ/mol that is obtained for a film without a plasticizer. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Solid polymer electrolyte; Plasticizer; Dibutylphthalate; Conductivity; Temperature studies; X-ray analysis

1. Introduction

Polymer electrolytes are of considerable interest for application in many electrochemical devices such as cellular telephones, smart credit cards, etc. [1–4]. These devices require small, thin batteries which can be readily fabricated from polymer-electrolyte-based cells. Ionically conducting polymer electrolytes were first suggested by Fenton et al. [5] in 1973. These authors showed that complexes formed with poly(ethylene oxide) (PEO) and alkali metal salts exhibit high ionic conductivity at elevated temperature. Subsequently, these complexes were proposed by Armand et al. [6] as electrolytes for solid-state battery applications.

Extensive reviews discussing the formation, structure, morphology and transport theory of PEO complexes have been published [7,8]. Berthier et al. [9], established that the ionic conductivity in polymer electrolytes is related to the amorphous phase of the samples. One of the most successful approaches to increasing the amorphous nature, and

hence, the ionic conductivity, is to incorporate a suitable plasticizer into the polymer electrolyte film [10,11]. The low viscosity and high dielectric constant of these plasticizers effectively lower the potential barrier to ion transport and tend to dissociate ion pairs into anions and cations, resulting in higher conductivity [12]. A polymer electrolyte consisting of PEO, an alkali metal salt and poly(ethylene glycol dimethylether) (PEGDME) as plasticizer exhibited an ionic conductivity of about 10^{-4} S cm at 40°C [13]. Conductivity data on PEO electrolyte with PC as plasticizer were also reported by Munshi and Owens [14]. Ballard et al. [15] recently reported a conductivity of 8×10^{-4} S cm⁻¹ for a polymer electrolyte containing amorphous PEO and 50% PC. The conductivity of the polymer electrolyte (PEO)₂₀-LiAsF₆ has been considerably increased by incorporating esters such as Diethyl phthalate and dioctyl sebacate as plasticizers [16]. Tarascon et al. investigated a plastic rechargeable lithium-ion battery employing, dibutylphthalate (DBP) as a plasticizer in the copolymer electrolyte consisting of PVDF-HFP [17]. This paper reports the effect of the concentration of DBP as a plasticizer on the morphology and conductivity of a (PEO)₈-LiAsF₆ complex film by employing X-ray diffraction (XRD) and AC impedance techniques, respectively.

* Corresponding author.

2. Experimental

PEO (Aldrich, USA) with an average molecular weight of 4×10^6 was dried overnight at 50°C under vacuum, LiAsF_6 (Aldrich, USA) was used without further purification. Acetonitrile (Merck, Germany) was purified and stored over dry 4 Å molecular sieves (Union Carbide, USA). DBP (Merck) was used without further purification.

The appropriate weights of the PEO and LiAsF_6 in the

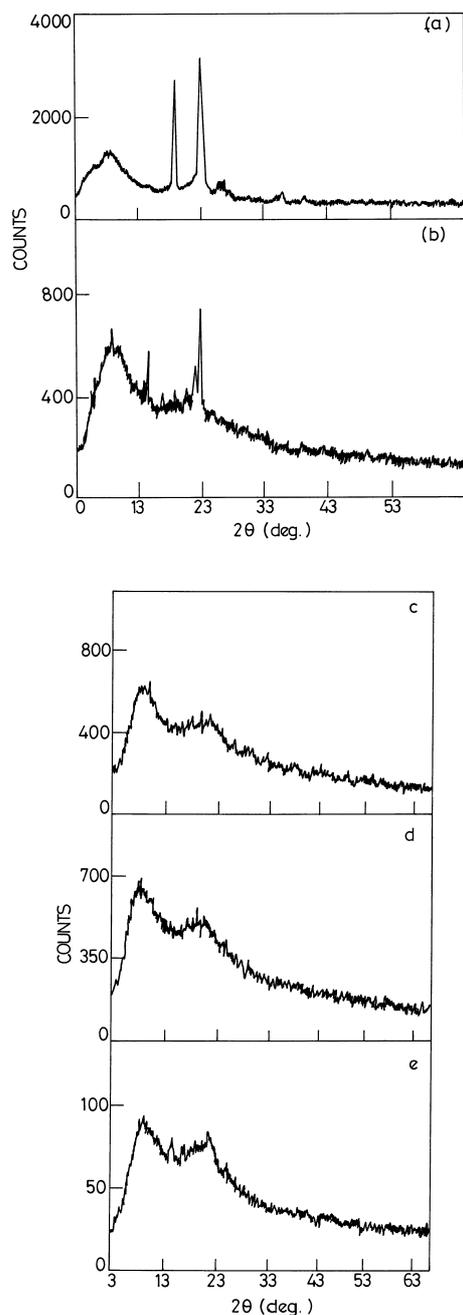


Fig. 1. XRD patterns for pure PEO, and polymer electrolyte blended with different plasticizer contents: (a) pure PEO; (b) $(\text{PEO})_8\text{-LiAsF}_6$:0.08 mol DBP; (c) $(\text{PEO})_8\text{-LiAsF}_6$:0.09 mol DBP; (d) $(\text{PEO})_8\text{-LiAsF}_6$:0.1 mol DBP; (e) $(\text{PEO})_8\text{-LiAsF}_6$:0.12 mol DBP.

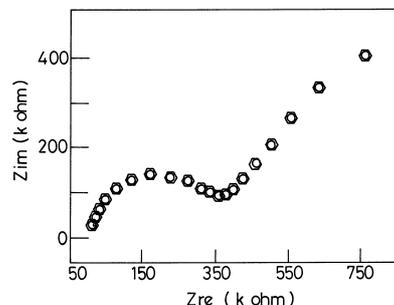


Fig. 2. AC impedance curve for $(\text{PEO})_8\text{-LiAsF}_6$ electrolyte.

ratio 8:1 [18] were dissolved in acetonitrile with various mole percentages of DBP. The solution was then stirred continuously until the mixture took on a homogeneous viscous liquid appearance. The mixture was then immediately cast on to a Teflon sheet container in a dry box and the acetonitrile allowed to evaporate completely. This procedure provided mechanically stable, free-standing and flexible films of thickness from 50 to 200 μm .

X-ray diffraction measurements were carried out on film samples at room temperature using $\text{CuK}\alpha$ radiation (Jeol JDX 8030, X-ray diffractometer, Japan) for 2θ values between 3 and 65° . Conductivity measurements were made for the polymer electrolytes by an AC two-terminal method using an EG&G Princeton Applied Research (PAR) Model 6310 Electrochemical Impedance Analyzer over a frequency range between 10 Hz and 100 KHz. The polymer electrolyte film was sandwiched between stainless-steel, ion-blocking electrodes, each of surface area 0.95 cm^2 , in a spring-loaded Teflon holder. A thermocouple was kept in close proximity to the electrolyte film for temperature measurement. The cell assembly was inserted into a wide-mouthed, glass reaction vessel. Film casting and cell assembly were performed in a vacuum-controlled, dry box. The ionic conductivity measurements were carried out for films containing different weight percentages of plasticizers and also for a film without plasticizer.

3. Results and discussion

3.1. XRD measurements

The XRD patterns for pure PEO and $(\text{PEO})_8\text{-LiAsF}_6$ films containing different contents of DBP are shown in Fig. 1. The well defined crystalline peaks observed for PEO show the presence of a significant proportion of a crystalline phase compared to an amorphous one. The

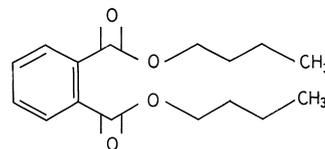


Fig. 3. Structure of dibutylphthalate (DBP).

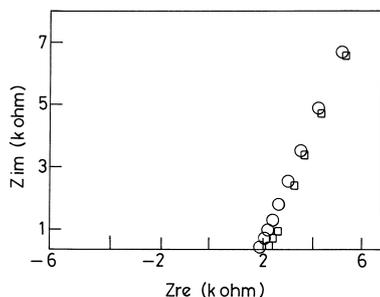


Fig. 4. Impedance plots for $(\text{PEO})_8\text{-LiAsF}_6\text{:0.09 mol DBP}$ (\square) and $(\text{PEO})_8\text{-LiAsF}_6\text{:0.1 mol DBP}$ (\circ).

patterns obtained for the electrolyte films $(\text{PEO})_8\text{-LiAsF}_6$ containing DBP also exhibit crystalline peaks, but the intensity of the peaks decreases and a broad spectrum appears as the plasticizer concentration is increased. This implies that the amorphous nature of the film increases with increase in concentration of DBP in the film. It is also observed that the $(\text{PEO})_8\text{-LiAsF}_6$ complex with 0.09 mol of DBP is devoid of crystalline peaks and exhibits only a broad spectrum which shows that its composition consists predominantly of an amorphous phase [19,20].

3.2. Conductivity measurements

The AC response for the electrolyte film $(\text{PEO})_8\text{-LiAsF}_6$ is depicted in Fig. 2. The high frequency semicircle yields information about the properties of the electrolyte such as bulk resistance, R_b , and bulk capacitance, C_b , which arise from the migration of lithium ions and the dielectric polarization of the polymer film, respectively. In the low frequency response region, the appearance of the non-vertical spike is attributed to the additional capacitance and resistance contribution arising out of dielectric relaxation and ion trapping in the $(\text{PEO})_8\text{-LiAsF}_6$ complex network [19,20]. The structure of DBP, which has been chosen as a plasticizing agent to the polymer electrolyte, is shown in Fig. 3. It is a low molecular weight aprotic polar additive with a high dielectric constant. The two oxygen sites in the

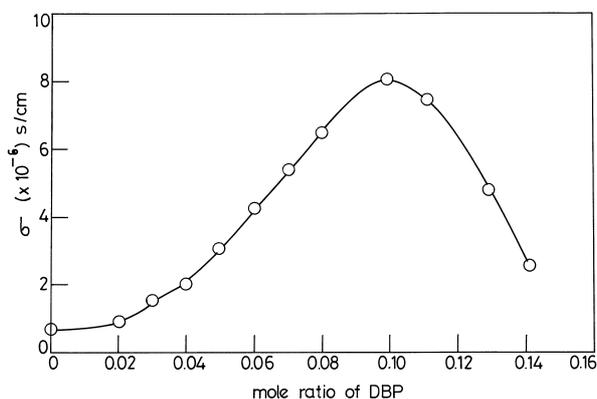


Fig. 5. Room temperature ionic conductivity of $(\text{PEO})_8\text{-LiAsF}_6$ with different contents of DBP.

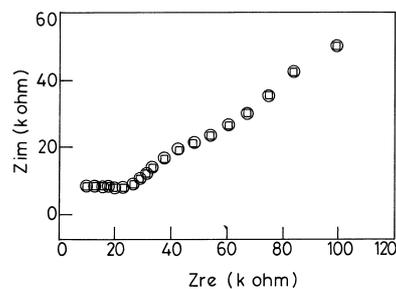


Fig. 6. Impedance diagram for $(\text{PEO})_8\text{-LiAsF}_6$ at 40°C .

ester linkages can provide co-ordination sites for Li^+ ion conduction through the film [16]. The impedance diagrams for $(\text{PEO})_8\text{-LiAsF}_6$ complex electrolyte films containing various compositions of DBP were obtained at room temperature; typical impedance plots for 0.09 and 0.1 mol of DBP are shown in Fig. 4. Fig. 5 shows that there is a slow rise in the conductivity value with plasticizer concentration followed by a steep rise in the values up to 0.09 mol of DBP with a maximum of $7.1 \times 10^{-6} \text{ S cm}^{-1}$ at 0.1 mol of DBP and then a rapid decline. Even though the electrolyte with 0.1 mol of DBP shows a high conductivity value, the oily appearance and non-free-standing nature of the film makes it unsuitable for any application. From this, it can be concluded that the electrolyte film with 0.09 mol of DBP is optimum from the point of view of its free-standing nature and reasonably high conductivity value of $6.4 \times 10^{-6} \text{ S cm}^{-1}$.

The XRD and AC impedance studies can be combined to explain the variation of conductivity with DBP concentration. The studies reveal that the amorphous nature of the film increases with increase in concentration of DBP up to 0.09 mol and, thereafter, the crystalline nature of the film increases. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte. The hopping of lithium-ions from one polymer segment to another is further facilitated by the presence of a liquid-like environment provided by the DBP. The appearance of higher conductivity from 0.09 to 0.1 mol DBP may be due to a contribution arising out of the fluidity caused by the DBP. Thereafter, the crystalline nature of the film predominates and causes a sharp fall in conductivity.

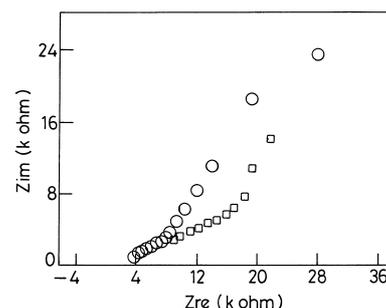


Fig. 7. Impedance diagrams for $(\text{PEO})_8\text{-LiAsF}_6$ at 55°C (\square) and at 65°C (\circ).

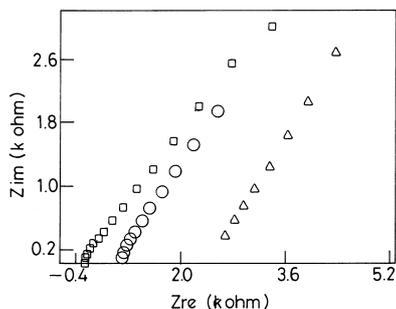


Fig. 8. Impedance diagram for $(\text{PEO})_8\text{-LiAsF}_6\text{:}0.09$ mol DBP at 40°C (Δ), 55°C (\circ) and 65°C (\square).

3.3. Temperature dependence of conductivity

Impedance diagrams for $(\text{PEO})_8\text{-LiAsF}_6$ and $(\text{PEO})_8\text{-LiAsF}_6\text{-(DBP)}_{0.09}$ were obtained at different temperatures, such as 40, 55 and 65°C , see Figs. 6–8. The temperature dependence of the conductivity (σ) of these systems obeys the Arrhenius Law. Curves of $\log_{10}\sigma$ vs. $1/T$ (Fig. 9) shows the temperature dependence of conductivity of $(\text{PEO})_8\text{-LiAsF}_6$ without plasticizer and of $(\text{PEO})_8\text{-LiAsF}_6$ with 0.09 mol of DBP. The activation energy (E_a) for both systems is calculated from the slope of the corresponding curves. The E_a for $(\text{PEO})_8\text{-LiAsF}_6$ is 10 kJ/mol, whereas the value for the film with 0.09 mole of DBP is reduced considerably to 0.578 kJ/mol.

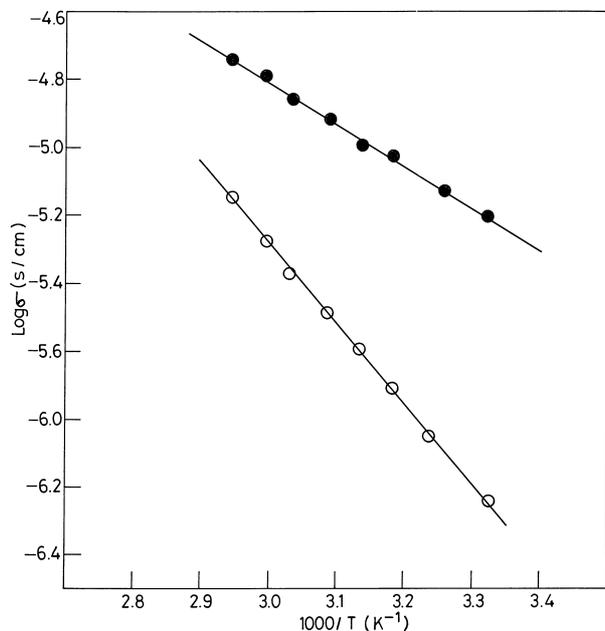


Fig. 9. Arrhenius plot for $(\text{PEO})_8\text{-LiAsF}_6$ (\circ) and $(\text{PEO})_8\text{-LiAsF}_6\text{:}0.09$ mol DBP (\bullet).

4. Summary

The polymer electrolyte containing 0.09 mol of DBP plasticizer produces a free-standing film with optimum conductivity. The increase in the conductivity with DBP addition of the polymer electrolyte is explained in terms of enhancement of the amorphous phase with concomitant reduction in the energy barrier to the segmental motion. This conforms with the observed low value of the activation energy calculated from the Arrhenius plot.

Acknowledgements

The authors wish to thank Mr. Athinarayanasamy, Dr. Pitchumani and Dr. Venkatachari for their helpful assistance with XRD and conductivity studies.

References

- [1] M. Armand, *Solid State Ionics* 69 (1994) 309.
- [2] B. Scrosati, in: B.V.R. Chowdari et al. (Eds.), *Solid State Materials*, World Scientific, Singapore, 1994, pp. 111–118.
- [3] P.R. Sorenson, T. Jacobsen, *Electrochim. Acta* 27 (1982) 1671.
- [4] Y. Aihara, M. Kodama, K. Nakahara, H. Okise, K. Marata, *J. Power Sources* 65 (1997) 143–147.
- [5] D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589.
- [6] M.B. Armand, J.M. Chabagno, M. Duclot, in: P. Vahista, J.N. Mundy, G.K. Shenoy (Eds.), *Fast Ion Transport in Solids*, Elsevier, North-Holland, New York, 1979, p. 131.
- [7] M.A. Ratner, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews—I*, Elsevier, New York, 1987, p. 173.
- [8] C.A. Vincent, *Electrochemical Science and Technology of Polymers—2*, Elsevier, New York, 1990, p. 47.
- [9] C. Berthier, W. Gorecki, M. Minier, M.B. Armand, J.M. Chabagno, P. Rigand, *Solid State Ionics* 11 (1983) 91.
- [10] E. Tsuchida, H. Ohno, K. Tsunemi, N. Kobayashi, *Solid State Ionics* 11 (1983) 227.
- [11] M. Gorecki, R. Andreani, C. Berthier, M.B. Armand, M. Mali, J. Roos, D. Brinkmann, *Solid State Ionics* 18 (1986) 295.
- [12] F.M. Gray, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Review—I*, Elsevier, New York, 1987, p. 139.
- [13] I.E. Kelly, J.R. Owen, B.C.H. Steele, *J. Power Sources* 14 (1985) 13.
- [14] M.Z.A. Munshi, B.B. Owens, *Solid State Ionics* 26 (1988) 41.
- [15] D.G.H. Ballard, P. Chesire, T.S. Mann, J.E. Przeworski, *Macromolecules* 23 (1990) 1256.
- [16] C.W. Walker Jr., M. Salomon, *J. Electrochem. Soc.* 140 (1993) 3409.
- [17] J.M. Tarascon, A.S. Gozdz, C. Schmutz, F. Shokoohi, P.C. Warren, in: B.V.R. Chowdari (Ed.), *Proceedings of the 10th International Conference on Solid State Ionics*, 86–88, 1996, 49.
- [18] P. Ferlohi, G. Chiodelli, A. Magistris, M. Sanesi, *Solid State Ionics* 18 and 19 (1986) 265–270.
- [19] P.V. Wright, C.C. Lee, *Polymer* 23 (1982) 681.