Ionic conductivities for poly(ethylene oxide) complexes with lithium salts of monobasic and dibasic acids and blends of poly(ethylene oxide) with lithium salts of anionic polymers*

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(Received 6 November 1983; revised 2 February 1984)

Lithium salts of two polyanionic addition polymers containing alkyl sulphonic acid and perfluoroalkyl carboxylic acid side groups were prepared. Blends of these polymers were formed with poly(ethylene oxide) (PEO). The blend containing alkyl sulphonate units showed some phase separation but this was not observed for the blend containing perfluoroalkyl carboxylate groups. In the latter case a comparatively high conductivity of $\sim 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 374 K was obtained. The anionic units in these blends are expected to be virtually immobile. Complexes formed from PEO and the Li-salt of hexafluoroglutaric acid had similar high ionic conductivities and there are grounds for supposing that the anions in these complexes may also be substantially immobilized. In addition, conductivity values were obtained for some PEO complexes containing lithium salts of some monobasic acids and it was found that the complex formed from the Li-salt of the strongest acid gave the highest conductivity ($\sim 4 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 373 K for a PEO–$LiSO_3CF_3$ complex).

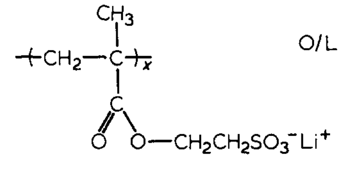
(Keywords: ionic conductivity; poly(ethylene oxide) complexes; lithium salts)

A number of previous publications[1-10] have reported high ionic conductivities for alkali metal salt–poly(ethylene oxide) (PEO) complexes. The alkali metal ions of these adducts are situated in an electron rich environment surrounded by the ether oxygens of the PEO chains. In these materials there are two mobile species; the cation and the anion. Transport numbers for lithium ions of ~0.5 were observed for a lithium thiocyanate–PEO complex by P. R. Sorenson and T. Jacobsen[6] and for a lithium trifluoromethyl sulphonate–PEO complex by J. R. Owen *et al.*[7]. Armand *et al.*[3] and Dupon *et al.*[8], however, consider in their earlier work that the major charge carrier is the cation.

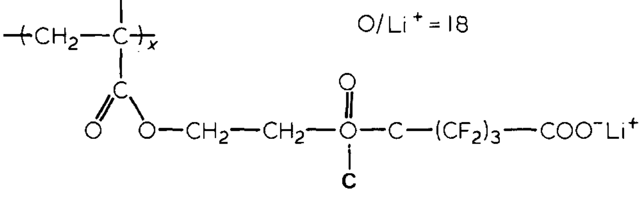
There is current interest in the construction of solid state batteries using such polymer–salt complexes as the electrolyte. The consequence of a transport number greater than zero for the anion is the existence of a diffusion potential and a substantial addition to the voltage across a polymer electrolyte through which a constant current is passed. Thus knowledge of the conductivity measured by a.c. techniques will in itself not give a true picture of the resistance of the electrolyte when it is used in a battery[6].

We propose that there are two simple ways in which a transport number for the Li^+-ion of unity or very close to unity may be achieved.

One is to incorporate the anion as part of a polymer chain. If the anions are chemically bound then their transport number will be zero and only the Li^+-ions will contribute to a permanent flow of charge. It is suggested in this paper that this may be achieved by producing blends of poly(ethylene oxide) with the lithium salts of anionic polymers. Providing the molecular weights of these salts are sufficiently high, the large size of the molecules will effectively immobilize the anionic groups. To obtain a low degree of ion-pairing[10] and have polymer blends with relatively high Li^+-ion conductivities, salts of anionic polymers derived from strongly acidic polymers were synthesized: poly(2-sulphoethyl methacrylate–Li salt) (PSEM-Li):


$O/Li^+ = 15$

and poly(2-(4-carboxyhexafluoro-butanoyl-oxy) ethyl methacrylate–Li salt) (PCHFEM-Li):


$O/Li^+ = 18$

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* Part of this work has been patented, UK Patent Number P8211145, entitled 'Solid State Electrochemical Cell'.

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(Salt concentrations are quoted as the ratio of the number of moles of oxygen atoms in PEO to the number of moles of Li^+-ions (O/Li^+)). Both these polymers have relatively long side chains which will help to reduce the steric hindrance for maximum interaction between the Li^+-ions and the PEO.

The second (more practically straightforward) method is to inhibit the mobility of the anion by use of a lithium salt of a dibasic acid, for example dilithium hexafluoroglutarate (LiHFG) $LiOOC(CF_2)_3COOLi$, as discussed below. The ionic conductivities are reported here and only a qualitative view of the anion immobility is given.

Conductivity values for a range of PEO complexes containing Li-salts of monobasic acids with anions of different sizes and stabilities were determined to compare the above materials.

EXPERIMENTAL

Preparation of materials

All the monobasic acids and hexafluoroglutaric acid were used as supplied by Fluorochemicals Ltd., and were neutralized in aqueous solution with lithium hydroxide. The water was removed on a rotary evaporator and the salts were dried by heating under vacuum at ~408 K for 24 h. The PEO used throughout this work was supplied by Aldrich Chemical Co. Ltd. with a molecular weight of 4×10^6 and was dried before use by storing over phosphorus pentoxide. Complexes with PEO were formed by dissolving the PEO and salt in methanol. The solvent was removed by evaporation, and residual solvent and water were removed by heating at 408 K under vacuum for 20 h or by heating at 383 K for a few days. The following salts of monobasic acids and their concentrations were used: lithium trifluoroacetate CF_3COOLi with $O/Li^+=4$, 9 and 18, lithium pentafluoropropionate CF_3CF_2COOLi with $O/Li^+=9$, lithium hepta fluorobutanoate $CF_3CF_2CF_2COOLi$ with $O/Li^+=9$ and 18, and lithium trifluoromethyl sulphonate CH_3SO_3Li with $O/Li^+=9$ and 18. The PEO–LiHFG complexes had salt concentrations O/Li^+ of 4, 9 and 18.

2-(4-Carboxy hexafluorobutanoyl-oxy) ethyl methacrylate was prepared by adding an excess of hexafluoroglutaric anhydride (b.p. 345 K) to dried 2-hydroxyethyl methacrylate in a sealed round bottomed flask flushed with nitrogen. The reaction vessel was left to stand for several hours before removing the excess anhydride by vacuum distillation at ~333 K. Polymerization was carried out in dried ethyl acetate in a sealed, degassed ampoule using benzoyl peroxide as initiator (~1% by weight of monomer). The ampoule was maintained at 363 K for 24 h to ensure almost complete decomposition of the peroxide. Since the polymer side chain is highly susceptible to hydrolysis, the polymer was prepared under conditions that would result in complete consumption of the monomer. Purification to remove unreacted monomer is thus unnecessary. Completion of polymerization was judged by appearance and texture alone. The polymer was neutralized in ethyl acetate with the stoichiometric amount of dried lithium methoxide. Methanol produced in this reaction was removed immediately to prevent transesterification of the polymer. To check that the conductivity results were not affected by free acid protons, two polymer samples were neutralized with a slight excess of base. Unreached LiOMe is easily removed as it is insoluble in ethyl acetate. A PCHFEM-Li/PEO blend was formed by adding a solution of PCHFEM-Li in ethyl acetate to PEO. This mixture was warmed in a closed environment to form a homogeneous phase and to prevent moisture contamination. Most of the solvent was removed on a rotary evaporator and last traces of solvent were removed by heating the blend under vacuum at 403 K for 20 h.

An impurity that could possibly contribute to the conductivity of the PCHFEM-Li/PEO blend is the lithium salt of hexafluoroglutaric acid. Traces of this dicarboxylic acid are present in industrially supplied hexafluoroglutaric anhydride. The maximum limit of all impurities for this chemical is 2% and such small amounts are expected to have a negligible effect on the ionic conductivity of the blend. The reactants and solvents used for the preparation of PCHFEM-Li were dried before use to prevent the production of hexafluoroglutaric acid by hydrolysis of the monomer or polymer. Neutralization of the fluorinated polymer did not result in the consumption of more than the anticipated amount of lithium methoxide and it was concluded that no hydrolysis had occurred. Drying the films in a vacuum oven at 403 K produced slight discolouration of the materials but the conductivity was not affected.

2-Sulphoethyl methacrylate as supplied by Polysciences Ltd. was neutralized in aqueous solutions of lithium hydroxide. The polymerization of the resulting salt was carried out in aqueous solution under nitrogen, by heating for one hour at 368 K using hydrogen peroxide as initiator. This method of polymerization produces a glassy polymer with a molecular weight of $>100\,000$[11]. A polymer blend was formed by dissolving the PSEM-Li in a 95% methanol/5% water mixture and adding a similar solution of PEO. After evaporation the residual solvent and last traces of moisture were removed by heating under vacuum at 408 K for 24 h.

Conductivity measurements

Films of the materials were obtained by pressing between hot plates at ~423 K. A central portion of each film was cut out and heated under vacuum at 403 K for 20 h to remove any possibility of contamination with moisture. Circular aluminium electrodes were deposited onto the surface of the films under a vacuum of 10^{-4} N m^{-2} using a Nanotech High Vacuum Coater.

Conductivity measurements were carried out in a thermally insulated box using a fast flowing stream of dry nitrogen to maintain the required temperature. Thermocouples positioned close to the samples were used to monitor and control the temperature of the films to an accuracy of better than ±0.5 K. Small brass plates placed above and below the films were used to provide electrical contact with the aluminium electrodes. The complex impedance of the samples was measured over the frequency range 100 mHz to 10 mHz using a Solartron 1172 frequency response analyser in the circuit shown in *Figure 1*. Essentially, the ratio of the voltages across the sample and measuring resistor, gives the ratio of the complex impedance of the sample to that of the standard resistor. The particular configuration chosen simplifies the correction for lead capacitance at high frequencies. The sample impedance Z can be calculated from:

$$Z=\frac{R'\left(\frac{V_y}{V_x}-1\right)}{(1+i\omega C_xR')}$$

where

$$R'=R_xR/(R_x+R)$$

The apparent conductivity was calculated from the real part of the admittance ($1/Z$) and the sample dimensions.

The measurement of conductivity over a range of frequencies was used to isolate the electrode effects. Since the electrodes are blocking to ions they cause an apparent reduction in conductivity and an increase in parallel capacitance at low frequencies, and measurements must be made at high enough frequencies for these effects to be negligible. A clear example of the effect is shown in *Figure 2* for a PCHFEM-Li/PEO blend of 2.5 mm thickness at 374 K. The identification of the low frequency dispersion with electrode effects is confirmed by a comparison of the results with those for a sample of the same material but a thickness of 0.29 mm at 375 K. These data for two physically different samples show similar conductivities at high frequencies but a shift in the frequency at which the low frequency dispersion occurs. This confirms that it is not a characteristic of the bulk material. In this work, conductivity values quoted were taken from the frequency independent region above the electrode dispersion. In general, the reproducibility of the measured conductivities for similar samples was better than 25%.

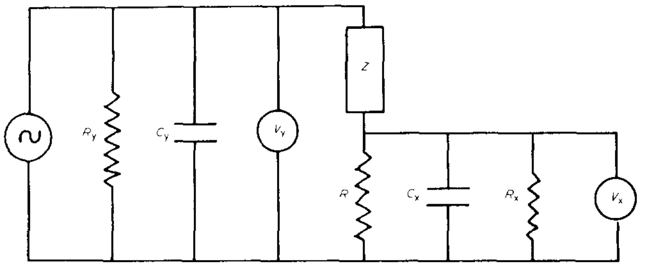

Figure 1 Impedance measuring circuit. V_x and V_y are measured by the frequency response analyser. C_x and C_y represent combined cable and input capacitance and resistance. Z is the sample impedance and R a standard resistor

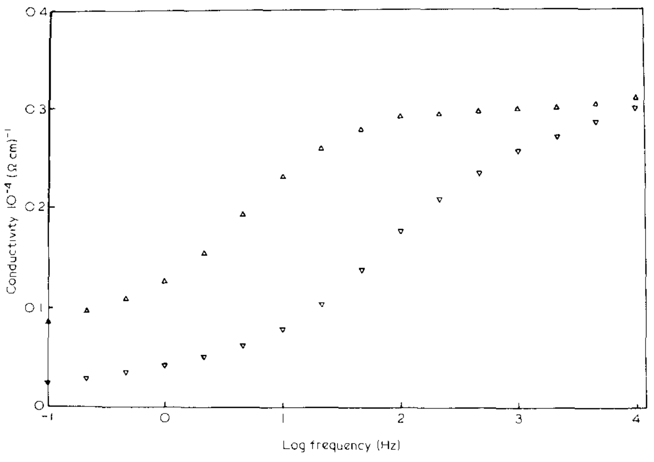

Figure 2 Apparent conductivity *versus* log frequency for two samples of PCHFEM-Li/PEO blend at 374 K, ▽, 0.29 mm thick, △, 2.52 mm thick. Note that the shift in low frequency dispersion showing it is not a bulk phenomenon

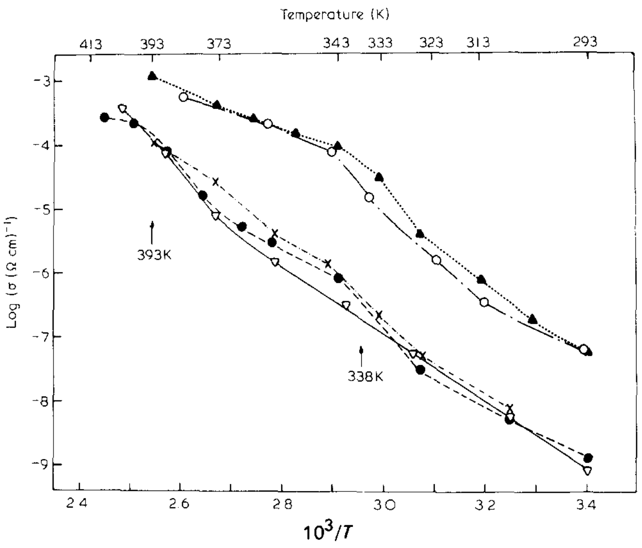

Figure 3 The logarithms of the conductivities against the reciprocal temperatures for PEO–CH_3COO Li complexes with O/Li^+=4 (▽), O/Li^+=9 (●), O/Li^+=18 (X), and for PEO–CF_3SO_3Li complexes with O/Li^+=9 (▲), O/Li^+=18 (○)

RESULTS AND DISCUSSION

Comparison of the PEO–CH_3COOLi and PEO–CF_3SO_3Li complexes

The results for the conductivity measurements on three PEO–CF_3COOLi complexes with O/Li^+=4, 9 and 18 and on two PEO–CF_3SO_3Li complexes with O/Li^+=9 and 18 are plotted in *Figure 3*. The knees in the conductivity plots at ~338 K for all the complexes except the PEO–CH_3COOLi complex with O/Li^+=4, correspond to crystalline melting of pure PEO or of PEO with a low salt content[10]. Alternatively Payne and Wright[5] have suggested that this may involve the disordering of a complexed interlamellar phase. The PEO–CH_3COOLi complex with O/Li^+=9 shows a second knee at ~393 K.

Traces resulting from a Differential Scanning Calorimetric (d.s.c.) investigation of the PEO–CH_3COOLi complexes are shown in *Figure 4*. The PEO–CF_3COOLi complex with O/Li^+=4 is saturated or almost saturated with salt[1–8] and has one melting endotherm at ~393 K. Melting points in the region of 393 K have previously been observed[10] for PEO–alkali metal salt complexes (with high salt concentration) but this melting temperature is low when compared with almost all other previously investigated PEO–alkali metal salt complexes containing high salt contents which have melting endotherms around 464 K[1–8]. D.s.c. analysis shows that at lower salt concentrations a further melting endotherm appears at ~338 K which increases in size as the salt content decreases. There is a corresponding reduction in the peak due to higher melting material. The transition at ~393 K corresponds with the knee in the conductivity plot for PEO–CF_3COOLi with O/Li^+=9.

The conductivity values obtained for PEO–CH_3SO_3Li complexes are several times higher than those for the PEO–CF_3COOLi complexes. This difference may be attributed to the greater stability of the trifluoromethyl sulphonate anion and a lower degree of ion-pairing. Trifluoromethyl sulphonate anion and a low degree of ion-pairing. Trifluoromethane sulphonic acid is often described as the strongest monobasic acid[12].

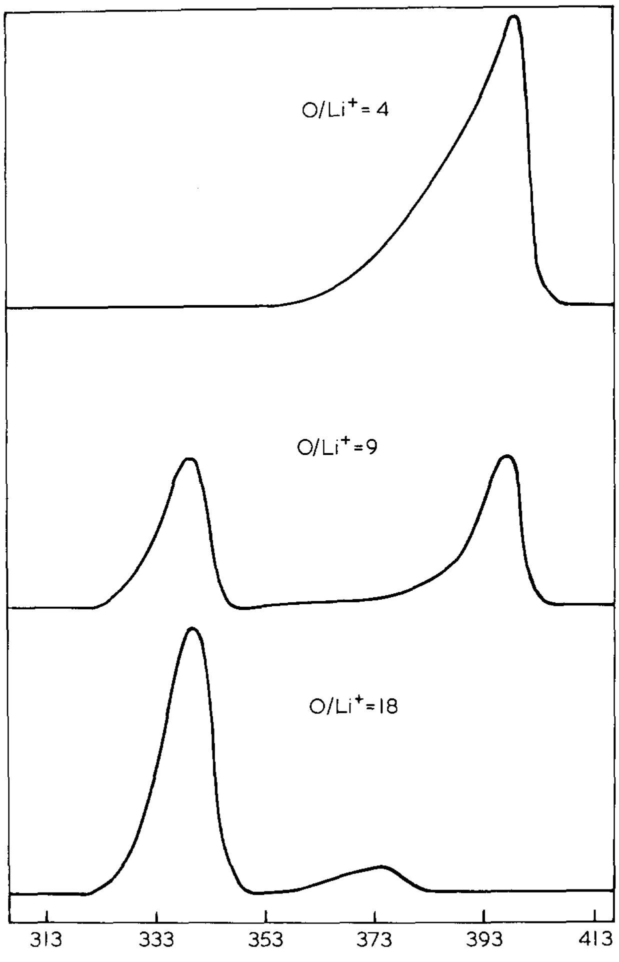

Figure 4 D.s.c. traces for CF_3COOLi–PEO complexes

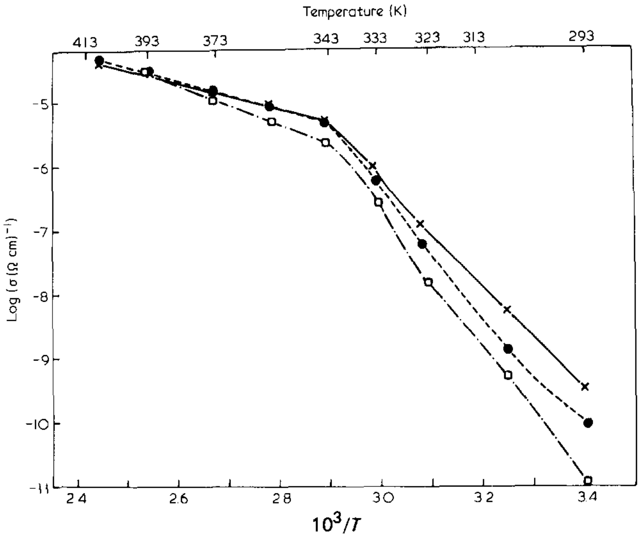

Figure 5 Log conductivities *versus* the reciprocal temperatures for PEO–LiHFG complexes with $O/Li^+ = 4$ (□), $O/Li^+ = 9$ (●), $O/Li^+ = 18$ (X)

Comparison of the PEO–LiHFG, PEO–CF_3COOLi, PEO–CF_3CF_2COOLi and PEO–$CF_3CF_2CF_2COOLi$ complexes

Figure 5 shows the results of the conductivity measurements for the PEO–LiHFG complexes with concentrations of $O/Li^+ = 4$, 9 and 18. A value of $\sim 3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at ~ 393 K was observed for all three concentrations. D.s.c. analysis of these materials shows only one melting endotherm at ~ 338 K and they are presumably amorphous above this temperature. The conductivity plots show the characteristic decrease in the activation energy for conduction above ~ 338 K which is observed for all unsaturated PEO–Li salt complexes, and may be ascribed to a sudden increase in the amount of amorphous material and an increase in the free volume. It was concluded from previous work that a high free volume was desirable for high ionic conductivities in polyether-alkali metal salt complexes[3,9]. A small decrease in the activation energy is also observed when the salt concentration is lowered.

The ionic conductivity results for PEO complexes with CF_3COOLi, CF_3CF_2COOLi and $CF_3CF_2CF_2COOLi$ all with $O/Li^+ = 9$ are plotted in *Figure 6*. There is only one major transition in the conductivity plots for the PEO–CF_3CF_2COOLi and the PEO–$CF_3CF_2CF_2COOLi$ complexes at ~ 338 K. Using *Figure 6*, conductivities for different complexes may be compared. Comparisons are best made at high temperatures where the results are not affected by the presence of crystalline material. When comparing the conductivity values for PEO complexes with Li-salts of different perfluorinated carboxylic acids a decrease in the conductivity with an increase in anoin size is observed (e.g. $2.9 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ for PEO–CF_3COOLi and $1.54 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ for PEO–$CF_3CF_2CF_2COOLi$ both at 409 K). This difference is not likely to be due to experimental error and may be due to one or a combination of the following three factors:

i) Small differences in the anion stability caused by different number of fluorines on the α and β carbon atoms of the salts which would affect the degree of ion-pairing.

ii) Increases in the size of the anion causing a significant reduction in its mobility.

iii) Differences in the volume fraction of PEO in the complexes.

These values are also compared in *Figure 6* with a PEO–LiHFG complex with $O/Li^+ = 9$ which has a value of $4.7 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 409 K. This result is $\sim 70\%$ lower than the lowest value observed for a lithium salt of a perfluorinated monobasic acid with the same salt concen-

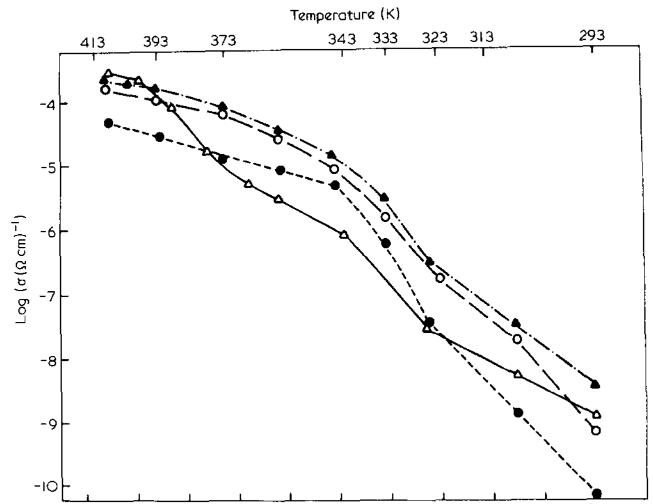

Figure 6 Logarithms of the conductivities against the reciprocal temperatures for a PEO–CF_3COOLi complex (△), a PEO–CF_3CF_2COOLi complex (▲), a PEO–$CF_3CF_2CF_2COOLi$ complex (○), and a PEO–Li HFG complex (●) all with $O/Li^+ = 9$

tration. The difference is believed to be partly due to the immobilization of the anion in the PEO–LiHFG complex. There are three considerations which together support this contention:

1) In PEO complexes with Li-salts of monobasic acids, the interaction between the anions and the PEO is only weak when compared with the interaction between the Li^+-ions and the PEO.

2) Recent work (at the University of Leeds[13] and elsewhere[10]) has shown that PEO–alkali metal salt complexes may have quite high degrees of ion pairing (>50%). This is dependent on the anion stability. For example, a perfluorinated carboxylic acid salt would be expected to have a relatively high degree of ion-pairing as indicated by the low conductivity of a PEO–CF_3COOLi complex when compared with a PEO–CF_3SO_3Li complex as shown in *Figure 3*[10].

3) In solution, one of the two cations of an alkali metal salt of a dibasic acid will become non ion-paired more readily than the second cation: the second cation will find it harder to dissociate to form a double negative charge. Consequently, in a PEO–LiHFG complex one of the two Li^+-ions of an LiHFG molecule is expected to impede the mobility of the anion by ion-pairing with the anion and simultaneously interacting with the ether oxygens of the PEO. The other complexing Li^+-ions of the same LiHFG molecule would dissociate from the anion and contribute to the flow of charge. An additional factor affecting the conductivity will arise if the PEO is complexing with molecules that have two ion-paired Li^+-ions. This will result in a lower free volume when compared with a complex containing a lithium salt of a monobasic acid with the same Li^+-ion concentration.

Polymer blends

Physical data. D.s.c. analysis of the polymer blends showed endotherms corresponding to crystalline melting of the PEO at ~338 K. Because these anionic polymer Li-salts were prepared by free radical polymerizations they would be expected to possess little stereoregularity and be essentially amorphous in structure. Therefore, in the blend with PEO, the anionic polymer-Li salt will form part of the amorphous phase. Above ~338 K there is no crystallinity in the blends. Similar systems have been reported previously. For example, E. Calahorra *et al.*[14] have studied the crystallization kinetics of blends of poly(ethylene oxide) with up to 40% poly(methyl methacrylate).

An unusual effect was observed when the PSEM-Li/PEO blend was heated above the melting temperature of the PEO in that the material became opaque. On cooling and subsequent recrystallization of the PEO the 'cloudiness' disappeared. A thin film was studied on the optical microscope between cross-polarizers and no birefringence was observed above ~338 K. The 'cloudiness' may be due to phase separation of the PSEM-Li (or of a PSEM/PEO complex) from the rest of the PEO. No phase separation was evident for the PCHFEM-Li/PEO blend. Lithium salts of perfluorinated carboxylic acids (analogous to PCHFEM–Li) form complexes with PEO but there are no reports of the formation of complexes with non-fluorinated alkyl sulphonic acids (analogous to PSEM-Li) that should have a lower anion stability.

Conductivity results. The results for the conductivity measurements on the polymer blends are plotted in *Figure 7*. Although the data for the PSEM-Li/PEO blend are difficult to interpret, values were obtained of $2.5\times10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 336 K and $6\times10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 387 K. The conductivity of the PCHFEM-Li/PEO blend is an order of magnitude greater than the conductivity of the PSEM-Li/PEO blends at the same temperature. This may be due to the different stabilities of the anions and their influence on the formation of complexes are discussed above. An additional feature of the PCHFEM-Li blend is that the Li^+-ions are situated further away from the polymer backbone, which therefore provides less steric hindrance to interaction with the PEO.

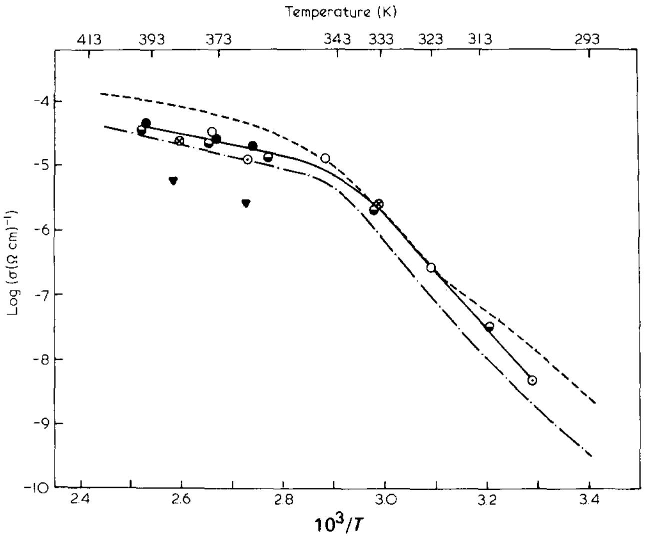

Figure 7 Log conductivities *versus* the reciprocal temperatures for PCHFEM–Li/PEO blends with thicknesses ranging from 0.29 mm to 2.52 mm (◒ ● ⊗ ⊙ ○) all with $O/Li^+=18$ and for a PSEM-Li/PEO blend with $O/Li^+=15$ (▼). Curves representing the conductivities for a PEO–$CF_3CF_2CF_2COOLi$ complex (– – – –) and for a PEO–LiHFG complex (–·–·–·) both with $O/Li^+=18$ are also shown

The results for the conductivity measurements on a PEO–$CF_3CF_2CF_2COOLi$ complex and on a PEO–LiHFG complex both with $O/Li^+=18$ are also shown in *Figure 7*. The values for the PCHFEM-Li/PEO blend at temperatures >353 K are on average ~60% lower than the results for a monobasic acid with similar anion stability and the same Li^+-ion concentration. On the other hand there is only an average difference of ~25% between the PCHFEM-Li/PEO blend and the PEO-LiHFG complex. These results are consistent with the immobilization of the anionic groups in the PCHFEM–Li/PEO blend. However, other possible influencing factors are a lower free volume for the blend provided by the stiffness of the PCHFEM-Li and a lower volume fraction of PEO in the blend.

Work is therefore continuing to verify the immobility of the anion in these complexes. Future work will also involve the use of perfluorinated dibasic acids containing one or two sulphonic acid groups to decrease the degree of ion-pairing and hence increase the ionic conductivity of the complexes with PEO, whilst maintaining anion immobility.

CONCLUSIONS

(1) Lithium salts of polyanionic addition polymers

containing strong acid groups, in which the anionic units are expected to be virtually immobile in terms of conductivity, can form blends with PEO that exhibit high ionic conductivities. Such behaviour has been demonstrated for a polymer containing perfluoroalkyl carboxylate units.

(2) Conductivity values are highest for those PEO complexes containing lithium salts derived from the strongest acids.

(3) Complexes formed from PEO and the lithium salt of hexafluoroglutaric acid have high ionic conductivities and there are grounds for supposing that in these materials the mobility of the anions has also been substantially reduced.

ACKNOWLEDGEMENTS

We wish to acknowledge helpful discussions with Dr W. J. Feast (University of Durham, UK) on the preparation of the fluorinated monomer. During part of this research, DJB was supported by an Advanced Battery Development Project funded by the Commission of the European Communities within the framework of the Energy Conservation R & D programme. We also wish to acknowledge helpful discussions with our colleagues at AERE Harwell, especially Drs R. M. Dell, A. Hooper and B. C. Tofield and with Dr J. R. Owen of Imperial College.

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