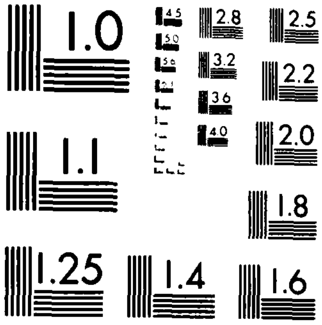
AD-A149 444 POLYMER ELECTROLYTES: AN INVESTIGATION OF SOME POLY (N-PROPYLAZIRIDINE)/L.. (U) ROYAL AIRCRAFT ESTABLISHMENT FARNBOROUGH (ENGLAND) K R BALDWIN ET AL. APR 84 1/1

UNCLASSIFIED RAE-TR-84036 DRIC-BR-93282 F/G 7/4 NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

BR93282

UNLIMITED

TR 84036

③

TR 84036

AD-A149 444

ROYAL AIRCRAFT ESTABLISHMENT

Technical Report 84036

April 1984

POLYMER ELECTROLYTES: AN INVESTIGATION OF SOME POLY (N-PROPYLAZIRIDINE)/LITHIUM SALT COMPOSITIONS

by

K. R. Baldwin
A. J. Golder
J. Knight

Procurement Executive, Ministry of Defence
Farnborough, Hants

84 12 18 149

REPRODUCED AT GOVERNMENT EXPENSE

REPORT DOCUMENTATION PAGE

Overall security classification of this page

UNCLASSIFIED

As far as possible this page should contain only unclassified information. If it is necessary to enter classified information, the box above must be marked to indicate the classification, e.g. Restricted, Confidential or Secret.

1. DRIC Reference (to be added by DRIC)	2. Originator's Reference RAE TR 84036	3. Agency Reference N/A	4. Report Security Classification/Marking UNCLASSIFIED

5. DRIC Code for Originator 7673000W	6. Originator (Corporate Author) Name and Location Royal Aircraft Establishment, Farnborough, Hants, UK
5a. Sponsoring Agency's Code N/A	6a. Sponsoring Agency (Contract Authority) Name and Location N/A

7. Title Polymer electrolytes: an investigation of some poly(N-propylaziridine)/lithium salt compositions.

7a. (For Translations) Title in Foreign Language

7b. (For Conference Papers) Title, Place and Date of Conference

8. Author 1. Surname, Initials Baldwin, K.R.	9a. Author 2 Golder, A.J.	9b. Authors 3, 4 .... Knight, J.	10. Date April 1984	Pages 24	Refs. 19
11. Contract Number N/A	12. Period N/A	13. Project	14. Other Reference Nos. Materials/Structures 81		

15. Distribution statement

(a) Controlled by - Head of Materials and Structures Department, RAE(F)

(b) Special limitations (if any) - None

16. Descriptors (Keywords) (Descriptors marked * are selected from TEST)

Polymer electrolyte conductivity solid-state battery.

17. Abstract

Some poly(N-propylaziridine)/lithium salt compositions have been synthesised and their electrical conductivities have been measured in order to assess their suitability as electrolytes in safe, leakproof, high energy-density lithium batteries operating at ambient temperature. The effects on conductivity of temperature, and the nature and concentration of the salt have also been studied.

The presence of the salts markedly improved the conductivity of the compositions over that of the undoped polymer but they were insufficiently conducting to be considered as battery electrolytes, due possibly to ion-pairing. Their creep resistance was also low.

It was concluded that less fluid compositions containing higher molecular weight polymers better able to promote ion separation would be more suitable.

F5910/1

RAE Form A143

UDC 621.3.035.4 : 678.4/.8 : 621.355.9

ROYAL AIRCRAFT ESTABLISHMENT

Technical Report 84036

Received for printing 9 April 1984

POLYMER ELECTROLYTES: AN INVESTIGATION OF SOME POLY(N-PROPYLAZIRIDINE)/LITHIUM SALT COMPOSITIONS

by

K. R. Baldwin

A. J. Golder

J. Knight

SUMMARY

Some poly(N-propylaziridine)/lithium salt compositions have been synthesised and their electrical conductivities have been measured in order to assess their suitability as electrolytes in safe, leakproof, high energy-density lithium batteries operating at ambient temperature. The effects on conductivity of temperature, and the nature and concentration of the salt have also been studied.

The presence of the salts markedly improved the conductivity of the compositions over that of the undoped polymer but they were insufficiently conducting to be considered as battery electrolytes, due possibly to ion-pairing. Their creep resistance was also low.

It was concluded that less fluid compositions containing higher molecular weight polymers better able to promote ion separation would be more suitable.

Departmental Reference: Materials/Structures 81

LIST OF CONTENTS

1 INTRODUCTION

In recent years, considerable improvements in some aspects of the performance of batteries over traditional types such as the Léclanché and lead-acid have been achieved using lithium anodes and improved cathode materials. Advances have occurred in energy- and power-densities and also in shelf lives, but the use of lithium necessitates the substitution of aqueous electrolytes by the less conductive organic aprotic electrolytes containing solvents such as propylene carbonate or dimethoxyethane. A disadvantage of using liquid solvents is that they may leak and since they are often inflammable, they constitute a hazard, especially if they lead to ignition of the lithium anodes. Problems have also occurred during the attempted recharging of secondary lithium batteries using organic liquid electrolytes due partly to their instability to the highly reactive deposited lithium.

In general, the conductivity of lithium ions through solid electrolytes is lower than that through liquids, but if the solid electrolyte can be easily manufactured in a flexible film form of thickness 10-100 μm, it could still be attractive for use in those high energy-density, low current-drain batteries where safety, absence of leakage and extra long shelf-life are desired. Several inorganic crystalline and glassy solids have been considered for such applications but they tend to be inflexible and until now have not been easily made in thin film form. The discovery in 1973 [1] that poly(ethylene oxide), PEO, complexed certain alkali metal salts and the subsequent realisation by Armand[2] that the relatively high ionic conductivities of the complexes above 100°C might make them useful in advanced batteries offered the prospect of providing a flexible solid crystalline electrolyte having the following properties:

(i) an adequate lithium ion conductivity above 100°C to sustain current withdrawal at densities in the range 0.1 to 1 mA/cm^2,

(ii) good kinetic stability of the electrolyte in contact with the electrode materials,

(iii) an electrolyte/electrode interface stable over many charge/discharge cycles.

These properties have been realised in practice and the cycling of cells of configuration

Li metal anode PEO-$LiCF_3SO_3$ electrolyte composite V_6O_{13} cathode

has recently been demonstrated[3]. [$LiCF_3SO_3$ is lithium trifluoromethanesulphonate.]

Recent research at RAE[4] and elsewhere on polymer electrolytes has been concerned with their intended use at temperatures below 70°C. In this range, PEO/$LiCF_3SO_3$ electrolyte is unsatisfactory for three reasons:

(1) Its conductivity is too low for continuous cell operation at a practical current density unless extremely thin films can be used.

(2) As the annealed electrolyte is cooled below the melting point of PEO (about 65°C), a crystalline phase tends to form whose proportion increases with

further cooling at the expense of an amorphous PEO - salt phase. Since it is now widely accepted[5] that the amorphous and not the crystalline phase is responsible for the fast ion conduction, the overall conductivity is further decreased below that expected for a totally amorphous electrolyte at the same temperature.

(3) Recent evidence[6] suggests that only about half of the charge in the electrolyte is carried by the lithium cations, and not the whole of it as originally anticipated. Thus not only is the current density further decreased but local depletion of lithium ions near the cathode or local precipitation of salt in the electrolyte could impair cell operation.

The current RAE intra- and extramural research programme attempts to prepare usable polymer electrolytes for ambient temperature operation by increasing their conductivity towards a 10^{-4} ohm^{-1} cm^{-1} target level before investigating their interaction with suitable electrode materials. The conductivity improvement is being sought both by modification of the existing PEO-based electrolyte and also by evaluating the electrical and mechanical properties of other polymers capable of incorporating lithium salts.

Despite the growing international interest in the structure of the polyether/salt complexes, the mechanism of conduction of the ions has not been fully established. In the absence of other coordinating molecules, the polymer itself must coordinate the cations of the added salt and this interaction must be sufficient to overcome the lattice energy of the salt. However the optimum strength of interaction between cation and polymer to obtain the highest cation mobility is not yet known so it was of interest to study a polymer analogous to PEO but in which the cation-polymer interaction was expected to be stronger. The polymer chosen for study was poly(N-propylaziridine) (PPA), $-\!\!\left[CH_2CH_2-N(C_3H_7) \right]\!\!-_n$, which is a nitrogen analogue of PEO. This class of polymer is not commercially available and so a sample was synthesised by a modification of a literature method (section 2). The N-propyl derivative was chosen for preparation because of the commercial availability in high purity of the 2-ethyl-2-oxazoline starting material. PPA was regarded as a suitable candidate for study for the following reasons:

(1) this type of polymer is known to form strong complexes with lithium salts[7],

(2) the N-alkylation makes the polymer aprotic and so its stability in contact with a lithium anode in a cell is likely to be higher than in poly(aziridine) itself,

(3) it contains a high density of potentially coordinating nitrogen atoms,

(4) being a tertiary amine, it should be very stable to reduction and moderately so to oxidation in the cell,

(5) it should have a low glass transition temperature making it flexible and the polymer chain segments mobile in the intended operating temperature range; a glass transition temperature of -50°C is quoted for the analogous N-methyl derivative[8] of molecular weight 11000,

(b) the pendant propyl groups are expected to make crystallisation less easy in the polymer/salt complex.

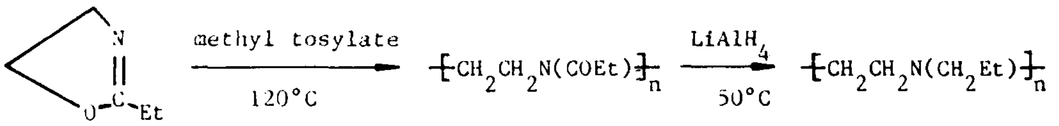
Section 2 summarises the preparative route to the polymer, further details of which are given in Appendix A. Section 3 describes the formation and properties of the polymer/salt compositions and section 4 describes their conductivity measurement and the results obtained. Section 5 compares these results with those previously obtained for other polymer electrolytes.

The electrical conductivity of a poly(N-methylaziridine)/lithium salt complex has been briefly mentioned in a patent[9] but few details were given.

2 SYNTHESIS OF POLY(N-PROPYLAZIRIDINE)

N-Alkylaziridines readily undergo ring-opening polymerisation in the presence of Lewis acid catalysts but the product polymers lack well-defined structures because of branching, formation of quaternary ammonium centres and possibly macrocyclic rings. Conversion of monomer is incomplete and the polymers may be contaminated with oligomers[10].

For these reasons, a sample of linear PPA was prepared in this work by the high-yield conversion of 2-ethyl-2-oxazoline to poly(N-propionylaziridine) according to the method of Bassiri[11], followed by the reduction of this intermediate polymer to the desired product by modifying the method of Saegusa[12]. The reactions may be represented as follows:



Preparative details are given in Appendix A. The product was a transparent pale yellow viscous syrup and its composition and structure were confirmed by elemental analysis, infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopy; no major impurities were present. An attempt to determine the molecular weight distribution of the polymer by gel permeation chromatography was unsuccessful due possibly to its strong adsorption on the column material. However a molecular weight average of only a few thousand is to be expected from literature reports[13] and this was supported by its NMR spectrum (Appendix A) in which several minor 'impurity' resonances could be attributed to a significant end-group concentration.

3 FORMATION AND NATURE OF POLYMER/SALT COMPOSITIONS

Direct spectroscopic evidence for the coordination of the lithium ion by polymers and its distribution therein has been difficult to obtain but was inferred in PEO/salt complexes by ^{7}Li NMR spectrosopy[5] and by extended X-ray absorption fine structure (EXAFS)[14]. However, evidence for polymer-salt interactions can also be obtained simply by observing the number of phases remaining after ensuring the intimate mixing of the carefully dried polymer and salt using a co-solvent and then completely removing the latter. Thus a sample of PPA (1.00 g) was dried by heating it under vacuum at 130°C for 2 hours and was treated, after cooling, with a solution containing 0.313 g of $LiClO_4$ in 6.6 g of tetrahydrofuran (THF) to give a 1:4 molar ratio of salt:polymer repeat unit. The salt was previously dried by heating it at 150°C for 6 hours in vacuo and the THF was freshly distilled from lithium aluminium hydride. When the solution was completely homogeneous, solvent was slowly removed under reduced pressure to ensure that none of the material escaped from the pre-weighed reaction vessel. The vessel and contents were then baked in vacuo at 150°C for 10 hours until the total weight of the contents was no more than 5 mg different from the sum of the weights of polymer and salt taken. This indicated virtually complete solvent removal and the product was a transparent yellow hard tough gum containing no solid lithium perchlorate phase. It was therefore concluded that, in the absence of coordinating species other than the polymer itself, an amorphous polymer/salt composition had been formed. The stoichiometry and phase limits of the complex were not further investigated.

Further solvent-free polymer-salt compositions were prepared in a similar manner, containing different salt:polymer repeat unit ratios in the range 1:1000 to 1:4. All preparations were carried out either in a glove-box containing air of water content 4 ppm by volume or under vacuum to minimise water absorption. THF solvent and lithium perchlorate were also dried before use. The resulting compositions were all transparent single-phase systems but their viscosities at 20°C increased markedly as the salt concentration increased, from viscous syrups similar to the undoped polymer at a 1:1000 stoichiometry through soft elastic gums at a 1:30 ratio to tough resins at more salt-rich levels. No quantitative viscosity data was obtained because insufficient material was available. This marked thickening effect during salt incorporation parallels that observed in the poly(propylene oxide)/lithium perchlorate system[15]. The present compositions were therefore mostly liquid-like and not suitable for casting as films on 'non-stick' surfaces by solvent evaporation from solutions. This was because of the difficulty of peeling them from the surface due to their strongly adhesive properties. For electrolyte film formation it was therefore found to be more satisfactory to either spread the composition directly onto the surface of one electrode at ambient temperature if it was mobile enough, or else to apply it when it had softened after heating. Complete coverage of the electrode surfaces was ensured by pressing the electrodes together until the composition just extruded around the whole perimeter of the narrow gap between the flat electrode faces. The 1:15 and 1:7 lithium perchlorate compositions needed to be applied and extruded whilst still hot; the analogous 1:4 composition remained glassy and impenetrable even at 150°C so no conductivity measurements could be made.

4 CONDUCTIVITY MEASUREMENTS

4.1 Procedure

The cell assembly (Fig 1) was placed in a glass tube in the glove-box and electrical and thermocouple connections sealed through the end of the tube enabled the electrolyte conductivity to be measured over a temperature range 20-100°C. Temperature was controlled by a Buchi TO-50 drying oven of which the glass tube formed the drying tube. The upper temperature was limited to 100°C because the temperature range of most interest for the present application was thereby covered and because the cell contained PTFE insulators and epoxy-resin joints which could degrade at higher temperatures. (Another cell allowing simultaneous electrolyte thickness and pressure measurements and operable over a wider temperature range is under construction).

After allowing the temperature of the cell to stabilise, the electrolyte resistance was estimated by recording the ac impedance of the cell and representing it in the complex plane using a Solartron 1250 frequency response analyser in conjunction with a Solartron 1186 electrochemical interface. Impedance measurements were made over a 50 kHz to 0.1 Hz frequency range decreasing at a rate of six logarithmic steps per decade, and using a 10 kΩ standard resistor for current measurement. The integration time was 5 seconds at each frequency. The sample temperature was then increased in steps of about 20°C and the resistance re-measured. Measurements taken over a 20-100-20°C cycle indicated virtually no hysteresis in the conductivity-temperature plots (see below) and suggested that the electrode separation did not change significantly during cycling. Impedance plots of the type shown in Fig 2 were obtained at the higher temperatures where the electrolyte conductivity was highest. Plots similar to Fig 3 were obtained at lower temperatures, and the semicircular portions at high frequencies approximated to the idealised model of the electrolyte resistance shunted with the geometric capacitance, enabling estimates of this and the dielectric constant to be made. The magnitude of the electrolyte resistance, R , was taken as the value measured along the z' axis at the point of intersection of it with the extrapolated low-frequency 'spike', as shown in the figures.

The electrolyte thickness, ℓ , was estimated optically at the end of the heating/cooling cycle and measurement of the electrode area A enabled the specific conductivity σ (ohm^{-1} cm^{-1}) to be calculated using the formula

$$\sigma = \frac{\ell}{AR} \ .$$

The estimated errors in the measured parameters were

electrolyte resistance, R (ohm)	±2%
temperature, T (kelvin)	0.2%
electrode area, A (cm^2)	up to 10% if alignment is poor
electrolyte thickness, ℓ (cm)	large, perhaps up to 20%.

Thus by far the largest uncertainty in the conductivity results was caused by the very crude estimation of electrolyte thickness using the present cell arrangement and by the fluid nature of the compositions. Other geometrical factors having a marked effect on accuracy were imperfections in the flatness and smoothness of the electrode surfaces, deviations from a perfectly parallel surface alignment and very slight non-coincidence of the electrode cylindrical axes. Thus conductivity measurements made at different temperatures for one sample during a temperature cycle can be compared with greater confidence than can the absolute magnitude of the conductivities of different samples at the same temperature, since the cell geometry did not significantly change during cycling.

4.2 Results

The impedance spectrum of the uncomplexed polymer consisted merely of a continuously increasing capacitative reactance as the frequency was decreased and so its specific conductivity was immeasurably low - less than 10^{-10} ohm^{-1} cm^{-1} at 20°C. The conductivities of several polymer/salt compositions are given in Table 1. They show a marked increase as the concentration of lithium perchlorate in them increases from zero, through a 1:100 stoichiometry, but reach a temperature-dependent maximum as the salt concentration increases over a 1:30 to 1:7 range, as shown in Fig 4 at different temperatures. The temperature-dependence of the conductivity is plotted in Arrhenius form in Fig 5. The temperature range was too limited to be able to distinguish clearly between Arrhenius and free-volume models for the conduction process but the conductivity-temperature behaviour of most compositions approximates to the linear Arrhenius form, enabling activation energies to be calculated. These are also indicated in Table 1 for each composition together with averaged estimated values for the geometrical capacitance (C_g) and dielectric constant (ε) of each electrolyte. These values were estimated from the frequencies f^* corresponding to the points of maximum reactance in the semicircular portions of the impedance plots of the compositions (see Fig 3) using the formulae:

$$C_g = \frac{1}{2\pi f^* R} \quad \text{and} \quad \varepsilon = \frac{\ell C_g}{\varepsilon_0 A} = \frac{\sigma}{2\pi f^* \varepsilon_0}$$

where ε_0 is the permittivity of free space (8.85×10^{-14} farad/cm).

Both the activation energies and the geometrical capacitances increased as the salt concentration increased and the compositions became tougher, the activation energy rising from about 20-30 kJ/mol and the capacitance from about 25-170 pF over the studied range.

The effect on conductivity of different anion shape was also studied by preparing a 1:20 composition containing $LiCF_3SO_3$ in place of the perchlorate salt, using a procedure similar to that described in section 3 but with acetonitrile as co-solvent (Appendix B). Its conductivity at 20°C (Table 1) appeared slightly, though not very significantly, higher than comparable $LiClO_4$ compositions, but any slight advantage appeared to be lost at higher temperatures because of the lower activation energy. This material was slightly less viscous at a given temperature than the analogous 1:15 and 1:30 $LiClO_4$ compositions.

5 DISCUSSION

It was intended that the above polymer/salt compositions, though liquid-like in not possessing any long-range ordering, should at least show some resistance to flow over the whole of the measured temperature range. However, they all tended to flow under applied pressure at 100°C, and even at 20°C in the case of the dilute complexes, so that all measurements were done under essentially zero load. These materials can thus be compared both with solutions of lithium salts in aprotic organic solvents such as 1,2-dimethoxyethane, and also with lithium perchlorate solutions in other coordinating liquid polymers such as poly(propylene oxide), PPO, of low molecular weight[15]. The former typically show conductivities of the order of 10^{-2} ohm^{-1} cm^{-1} at 25°C, whilst the corresponding values for the latter and for the present $LiClO_4$/PPA materials reach maxima of the order of 10^{-5} and 10^{-8} respectively (see Fig 4). The PPA studied in this work, being a tertiary amine polymer, is one of the closest nitrogen analogues of the polyethers of which PPO is an example. Not surprisingly therefore the behaviour of the two polymers after incorporation of $LiClO_4$ is very similar in:

(1) the dependence of the conductivity on salt concentration,

(2) the shift of the conductivity maxima to higher salt concentrations with an increase in temperature (from about 1:20 at 25°C to about 1:10 at 100°C for PPA),

(3) the marked increase in viscosity of the compositions with an increase in salt concentration,

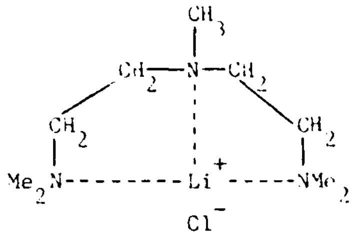
(4) the increase in Arrhenius activation energy with increasing salt concentration in this study and one on an analogous block copolymer system containing propylene oxide sequences[16],

(5) the slight improvement in conductivity obtained at low temperature by substituting $LiClO_4$ by $LiCF_3SO_3$ (again comparing this work with that on the above block copolymer).

Following these analogies, it is reasonable to assume that the conductivity of the $LiClO_4$/PPA compositions, already 1000-fold less than their PPO analogues, would be even lower if their creep resistance could be improved by the use of a polymer of higher molecular weight, since such a decrease was found for the PPO/lithium salt system[15].

The much lower conductivity of the PPA/salt system compared with the PPO/salt complexes could be due to the existence of strong ion-pairing in the former, rather than simply to the stronger polymer-cation interaction. This is because the anions should still be freely mobile and conducting in the case where the lithium cations are totally enveloped by chelation with the polymer amine groups. However the formation of ion pairs in the present work is more difficult to envisage because of the excess of coordinating nitrogen atoms above the presumed maximum four-fold coordination around the lithium ion and because of the lower tendency for anions such as perchlorate to ion-pair, as compared to halide ions.

Ion-pairing is known to decrease the conductivity of PEO/sodium borohydride complexes[17] and was postulated in oligomeric analogues[7] of the PPA/salt compositions to explain their unusually high solubility in hydrocarbons. The structure of a complex formed between lithium chloride and a tridentate amine was believed to be



and evidence for the strength of the cation-polymer interaction was obtained from the NMR spectra of the solutions[18]. The conductivity of the analogous bromide complex was claimed to be as high as 5.2×10^{-4} ohm^{-1} cm^{-1} in the molten state at 110°C. The same patent[7] also described the formation of a 1:3 complex between lithium bromide and poly(N-methylaziridine) of molecular weight 10000 but this was hydrocarbon-insoluble and no conductivity data was given.

It is also noteworthy that the poor conductivities of the PPA/salt compositions compared to those of the polyether/salt complexes are not attributable to low dielectric constant values since they are similar in magnitude to those found for both PEO/LiSCN complexes ($\varepsilon = 17$)[6] and PPO/zinc chloride complexes ($\varepsilon = 20$).

The conductivity-temperature behaviour of the 1:15 $LiClO_4$/PPA composition is compared in Fig 6 with published data on a variety of lithium salt/polymer compositions by different authors. Clearly the conductivity of this complex lies near the bottom end of the observed range, though it is equally as conducting at 20°C as several of the complexes of LiSCN or $LiCF_3SO_3$ with PEO and PPO. It is also apparent that the only compositions whose conductivities presently exceed 10^{-6} ohm^{-1} cm^{-1} at 20°C are those containing either solvents such as propylene carbonate or ones made from low-molecular-weight liquid polymers giving very fluid polymer/salt compositions. The so-called 'high-purity' amorphous $LiClO_4$/PEO complexes are almost as conducting but since this is believed to be due to the presence of traces of water[19], they are probably unsuitable as battery electrolytes. Poly(ether-urethane) gels containing $LiClO_4$ without other solvents were very poor conductors.

6 CONCLUSIONS

(i) A low molecular weight liquid poly(N-propylaziridine) formed single-phase amorphous compositions with lithium perchlorate over a range of stoichiometries from 1:1000 to 1:4, based on the molar ratio of the salt:polymer repeat unit.

(ii) As the salt concentration in the polymer was increased both the viscosity and the electrical conductivity of the compositions increased. However the conductivity reached its maximum at 25°C at about a 1:20 stoichiometry when the material was a soft gum, becoming slightly less conducting as the consistency became tough and resinous with further salt addition.

(iii) An analogous 1:20 $LiCF_3SO_3$:polymer composition was slightly more conducting at 20° but less so at higher temperatures.

(iv) The best conductivity of about 9×10^{-9} ohm^{-1} cm^{-1} at 25°C was comparable with those of some $LiCF_3SO_3$/poly(ethylene oxide) complexes but the conductivity was lower than the latter at higher temperatures and the compositions were also more susceptible to creep.

(v) The poly(N-propylaziridine)/lithium salt compositions were electrically and mechanically unsuitable as 'solid' electrolytes for lithium batteries operating at ambient temperature.

(vi) The low conductivities of the present materials were believed to be due to ion-pairing and their relatively high fluidity to the low molecular weight of the polymer. Further work on polymer electrolytes should therefore concentrate on using higher molecular-weight polymers better able to promote ion separation and mobility.

Acknowledgment

We thank Dr A. Cunliffe, PERME Waltham Abbey, for the NMR characterisation of the polymer.

Appendix A

SYNTHESIS AND CHARACTERISATION OF POLYMERS

(see section 2)

Poly(N-propionylaziridine)

2-Ethyl-2-oxazoline (Aldrich, 99%, used as received) was deoxygenated and 312 g was then treated with methyl p-toluenesulphonate (Aldrich, 0.25 g) at ambient temperature. The solution was then heated at 120°C for 20 hours under a nitrogen atmosphere. There was no evidence of polymerisation so a further aliquot (0.16 g) of initiator was added after cooling. After a further period of 2 hours at 120°C an exothermic polymerisation reaction occurred which continued for 1 hour without the need for external heating. The temperature was maintained at 120°C for a further 2 hours using an oil bath to ensure complete conversion and the reaction mixture was then cooled slowly to 20°C. The tough gummy product was dissolved over several days in dichloromethane which had previously been dried by distillation from lithium aluminium hydride and the solvent weight was adjusted to give a 30 wt% stock solution of poly(N-propionylaziridine).

Tests showed that the product was dissolved or swollen by the majority of common organic solvents but could be precipitated from solution by n-hexane or diethyl ether. However, in both cases, it precipitated in a slightly swollen state as a gum. Diethyl ether was the more satisfactory precipitant and so the polymer was purified in portions by slowly adding the dichloromethane concentrate into an excess of vigorously stirred diethyl ether. The gummy precipitate was washed with ether then dried in a vacuum oven at 40°C over one week. The resulting brittle foamy mass could then be powdered to facilitate further drying as above. Yield = 80%. Analysis:

required for C_5H_9NO - 60.6%C; 9.15%H; 14.1%N

found - 59.2%C; 9.1%H; 13.7%N .

No significant endothermic events were observed in the differential scanning calorimeter plots of the pure polymer in the temperature range -35 to 250°C, apart from very small endotherms at 148 and 233°C. The melting transition at 148°C could be reproduced on a larger scale by observing the softening and fusion of the white solid into a transparent mass at approximately this temperature. The transition therefore occurred in the range expected (140-210°C) for this type of polymer[11]. The infra-red (IR) spectrum of the polymer (Table 2) is similar to that previously reported for poly(N-acylaziridines) and shows a strong amide carbonyl absorption at 1640 cm^{-1}.

Poly(N-propylaziridine)

The reduction of the acyl polymer was carried out exclusively in tetrahydrofuran since previous tests had shown this to be a good solvent for the polymer, in contrast to an earlier finding[12]. A sample of the dried acyl polymer (54 g) was dissolved in tetrahydrofuran (1120 g) which was freshly distilled from lithium aluminium hydride. The solution was deaerated in a three-necked flask and a slurry of lithium aluminium hydride (18.5 g) in dry tetrahydrofuran (40 g) was added to the stirred solution against a counter-current of nitrogen. A gelatinous precipitate formed immediately which prevented efficient stirring and the mixture was then maintained at 50°C for two days under nitrogen. After this time, the gel remained and a further 6 g of hydride was added. Heating was continued for a further 15 hours. After cooling to ambient temperature, the mixture was hydrolysed in portions by transferring it to a large beaker maintained in an ice-bath and adding distilled water dropwise to the vigorously stirred mixture. The gel dissolved and a fine white suspension formed which was filtered off. Solvent was removed from the filtrate in a rotary evaporator and the viscous product was dissolved in n-hexane, centrifuged to remove residual solid and stripped of solvent under vacuum yielding 26 g of viscous liquid poly(N-propylaziridine). Analysis:

required for $C_5H_{11}N$ - 70.5%C; 13.0%H; 16.5%N
found - 69.5%C; 12.5%H; 16.9%N
(total 98.9%) .

An attempt was made to purify a portion of the product according to the acid extraction procedure of Saegusa[12] but the recovered yield was low and the acidified polymer was found to be highly susceptible to complex formation with metal ions yielding insoluble products. Polymer/salt compositions were therefore prepared directly from the crude product.

The IR spectrum of the polymer (Table 2) was similar to that previously recorded for the analogous ethyl polymer as well as to the model compound tetraethylethylenediamine[12], and differs from the spectrum of the acyl derivative in showing virtually no absorptions in either the 3000-4000 cm^{-1} range or in the carbonyl stretching region; a carbon-hydrogen stretching absorption is also shifted to lower frequency (2805 cm^{-1}) in the spectrum of the reduced polymer. Impurity absorptions present at 3310 and 1655 cm^{-1} could possibly be due to slight protonation of a few of the amine groups or to the presence of a trace of poly(aziridine) in the sample.

No endothermic events were observed during repeated differential scanning calorimetry cycling of the polymer over a -35 to 170°C range. Likewise, a polymer/lithium perchlorate composition showed no transitions over a -50 to 200°C range.

The ^1H NMR spectrum of poly(N-propylaziridine) (Table 3) confirmed its overall structure, showing four distinct resonances due to the four different proton environments at the expected chemical shifts. A ^{13}C NMR spectrum (decoupled) further exposed two sets of minor impurity resonances, one of which was probably associated with the $\left(CH_2N[CH(OH)C_2H_5]CH_2 \right)$ grouping and the other with polymer end-groups. The impurity peaks in the IR spectrum at 1655 and 3310 cm^{-1} could also be attributable to a hydroxyl group of the type indicated.

Appendix B

PREPARATION OF A POLY(N-PROPYLAZIRIDINE)/$LiCF_3SO_3$ COMPOSITION

(see section 4.2)

A crude sample of lithium trifluoromethanesulphonate (Ventron, 3.25 g) was purified by dissolving it in AR acetone (4.5 g) in a glove-box, centrifuging off the insoluble solid in a sealed tube, evaporating the clear filtrate to dryness and drying the resulting powder to constant weight in a vacuum drier at 100°C. This was combined with the dried solid from a second extraction yielding 1.8 g of solid which completely dissolved in acetone and acetonitrile.

A solution of 0.51 g of the salt in freshly dried acetonitrile was prepared, giving a total solution weight of 5.63 g. 0.86 g of this was mixed with 0.84 g of polymer in a short B19 test tube giving a 1:20 molar ratio of salt to polymer repeat units. A milky solution formed which cleared on evaporating the solvent and the resulting foamy mass softened on heating under vacuum to a clear pale yellow viscous liquid. The material was applied when still hot to the electrodes as described in section 3 above.

Table 1

ELECTRICAL DATA ON POLY(N-PROPYLAZIRIDINE)/SALT COMPOSITIONS

Salt	Salt:$C_5H_{11}N$ molar ratio	Temp. (°C)	Conductivity (ohm^{-1} cm^{-1})	Activation energy (kJ/mol)	Geometric capacitance (pF)	Dielectric constant
None	-	20	$< 10^{-10}$	-	25	11
$LiClO_4$	1:100	24	8.5×10^{-10}	20	39	18
		33	3.7×10^{-9}			
		39	5.2×10^{-9}			
		59	1.4×10^{-8}			
		80	4.4×10^{-8}			
		102	1.1×10^{-7}			
$LiClO_4$	1:30	23	5.9×10^{-9}	24.5	39	17
		32	1.5×10^{-8}			
		37.5	1.8×10^{-8}			
		48	4.4×10^{-8}			
		58.5	8.1×10^{-8}			
		69.5	1.6×10^{-7}			
		79	2.4×10^{-7}			
		100.5	6.3×10^{-7}			
$LiClO_4$	1:15	19	4.3×10^{-9}	33	77	13
		27.5	1.2×10^{-8}			
		37.5	2.1×10^{-8}			
		47	7.45×10^{-8}			
		57.5	1.3×10^{-7}			
		68.5	4.3×10^{-7}			
		78	5.9×10^{-7}			
		94	2.4×10^{-6}			
$LiClO_4$	1:7	29.5	6.0×10^{-9}	36	166	22
		41	3.0×10^{-8}			
		49	4.5×10^{-8}			
		59.5	1.5×10^{-7}			
		69.5	2.8×10^{-7}			
		83	1.25×10^{-6}			
		94	1.5×10^{-6}			
		105	4.3×10^{-6}			
$LiCF_3SO_3$	1:20	20.8	1.1×10^{-8}	22	100	16
		23.8	8.2×10^{-9}			
		38.7	3.2×10^{-8}			
		53.4	1.25×10^{-7}			
		58.1	1.19×10^{-7}			
		79.5	3.2×10^{-7}			
		91	6.8×10^{-7}			

Table 2

INFRA-RED SPECTRA OF POLYMERS

Polymer	Infra-red absorptions (cm^{-1})*
Poly(N-propionylaziridine)	3510mbr, 2980s, 2940s, 2880m, 1735wsh, 1640s, 1470s, 1425s, 1375s, 1320m, 1240m, 1200s, 1130w, 1080m, 1065s, 915w, 820m
Poly(N-propylaziridine)	3310vw, 2960s, 2940s, 2870s, 2805s, 1655w, 1465s, 1380m, 1365sh, 1340m, 1295mbr, 1115sh, 1075s, 1025m, 950w, 885w, 770wsh, 745w

* s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very

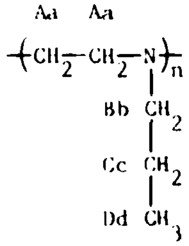
Table 3

NMR SPECTRA OF POLY(N-PROPYLAZIRIDINE)

Nucleus	Chemical shift*	Relative intensity	Assignment**	Remarks
^{1}H	2.55	87 (a + b)	a	singlet
	2.45	-	b	multiplet
	1.50	32	c	multiplet
	0.85	42	d	triplet
^{13}C (decoupled)	57.17		B	singlet
	52.95		A	"
	20.28		C	"
	11.67		D	"
	86.89	14% of A + B + C + D	end-groups plus minor impurities	
	56.79			
	54.46			
	51.10			
	47.05			
	31.33			
	22.39			
	13.89			
	8.69			

* tetramethylsilane = 0 for ^{1}H

** assignments refer to the following:



$$\left(\overset{Aa}{CH_2}-\overset{Aa}{CH_2}-N\right)_n \quad N-\underset{Bb}{CH_2}-\underset{Cc}{CH_2}-\underset{Dd}{CH_3}$$

REFERENCES

No.	Author	Title, etc
1	D.E. Fenton J.M. Parker P.V. Wright	Complexes of alkali metal ions with poly(ethylene oxide). Polymer, 14, 589 (1973)
2	M.B. Armand J.M. Chabagno M.J. Duclot	Poly-ethers as solid electrolytes. In "Fast ion transport in solids", edited by P. Vashishta, J.N. Mundy and G.K. Shenoy, North Holland, Amsterdam, p 131 (1979)
3	J.M. North A. Hooper	Fabrication and performance of all-solid-state polymer electrolyte-based rechargeable lithium cells. Paper presented at the Fourth International Conference on Solid State Ionics, Grenoble, July 1983
4	K.R. Baldwin J. Knight	Further studies of epoxy-cured polysulphide electrolytes. RAE Electrochemistry and Battery Technology Section, Battery Report 301
5	C. Berthier W. Gorecki M. Minier M.B. Armand J.M. Chabagno P. Rigaud	Microscopic investigation of ionic conductivity in alkali metal salts - poly(ethylene oxide) adducts. Solid State Ionics, 11, 91 (1983)
6	T. Jacobsen P.R. Sorensen	Conductivity, charge transfer and transport number - an ac investigation of the polymer electrolyte LiSCN-poly(ethylene oxide). Electrochimica Acta, 27, (12), 1671 (1982)
7	A.W. Langer T.A. Whitney	Inorganic lithium-amine complexes. US Patent 3,734,963 (1973)
8	V.A. Ponomarenko I.A. Chekulaeva E.Y. Gorodetskaya A.V. Ignatenko A.G. Kechina	Polymerisation of N-methylethyleneimine and N-methylpropyleneimine. Vys. Soed. B, 16, (11), 815-7 (1974)
9	M. Armand M. Duclot	Alkaline batteries with solid electrolytes. Patent Specification Fr. Demande 2,442,513 (1980)
10	O.C. Dermer G.E. Ham	"Ethyleneimine and other aziridines". Academic Press, New York, p 330 (1969)
11	T.G. Bassiri A. Levy M. Litt	Polymerisation of cyclic imino ethers I. oxazolines. Poly. Lett., 5, 871 (1967)
12	T. Saegusa A. Yamada H. Taoda S. Kobayashi	Linear poly(N-alkylethyleneimine)s. Macromolecules, 11, (2), 435 (1978)

REFERENCES (concluded)

No.	Author	Title, etc
13	T. Saegusa H. Ikeda H. Fujii	Isomerisation polymerisation of 2-oxazoline. IV, Kinetic study of 2-methyl-2-oxazoline polymerisation. Macromolecules, 5, (4), 359 (1972)
14	C.R.A. Catlow A.V. Chadwick G.N. Greaves L.M. Moroney	An EXAFS study of rubidium - poly(ethylene oxide) - salt complexes. Paper presented at the 4th International Conference on Solid State Ionics, Grenoble, July 1983
15	M. Watanabe J. Ikeda I. Shinohara	Effect of molecular weight of polymeric solvent on ion conductive behaviour in Poly(propylene oxide) solution in $LiClO_4$. Poly. J., 15, (1), 65 (1983)
16	M. Watanabe K. Nagaoka M. Kanba I. Shinohara	Ionic conductivity of polymeric solid electrolytes based on poly(propylene oxide) or poly(tetramethylene oxide). Poly. J., 14, (11), 877 (1982)
17	B.L. Papke R. Dupon M.A. Ratner D.F. Shriver	Ion-pairing in polyether solid electrolytes and its influence on ion transport. Solid State Ionics, 5, 685 (1981)
18	M.T. Melchior L.P. Klemann A.W. Langer	Magnetic resonance studies of polytertiary amine chelated alkali metal compounds. In "Polyamine-chelated alkali metal compounds", edited by A.W. Langer (Proc. Symp. New York, August 1972), Amer. Chem. Soc. Publication (1974)
19	J.E. Weston B.C.H. Steele	Effects of preparation method on properties of lithium salt - poly(ethylene oxide) polymer electrolytes. Solid State Ionics, 7, 81 (1982)

Key

1 Polished cylindrical stainless steel electrodes
2 Polymer electrolyte
3 Connecting leads
4 Cylindrical electrode PTFE seating
5 PTFE lead sheathing
6 Rectangular frame
7 Tightening nuts

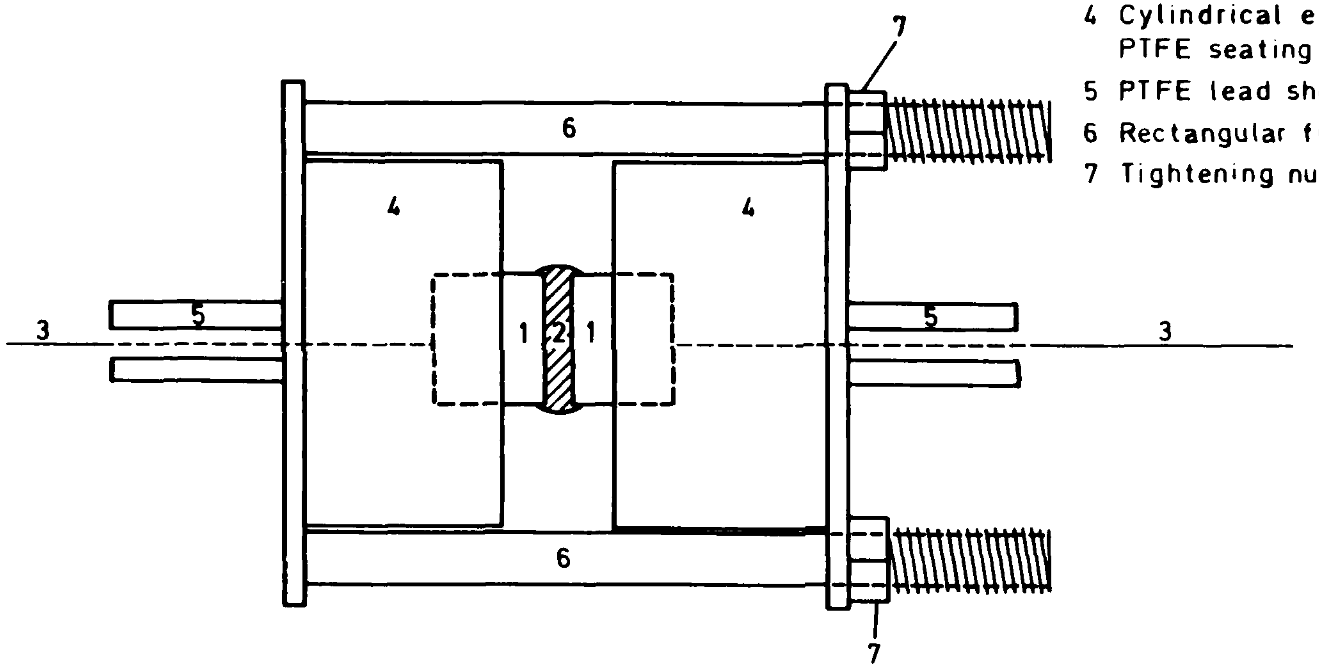


Fig 1 Conductivity cell configuration (schematic)

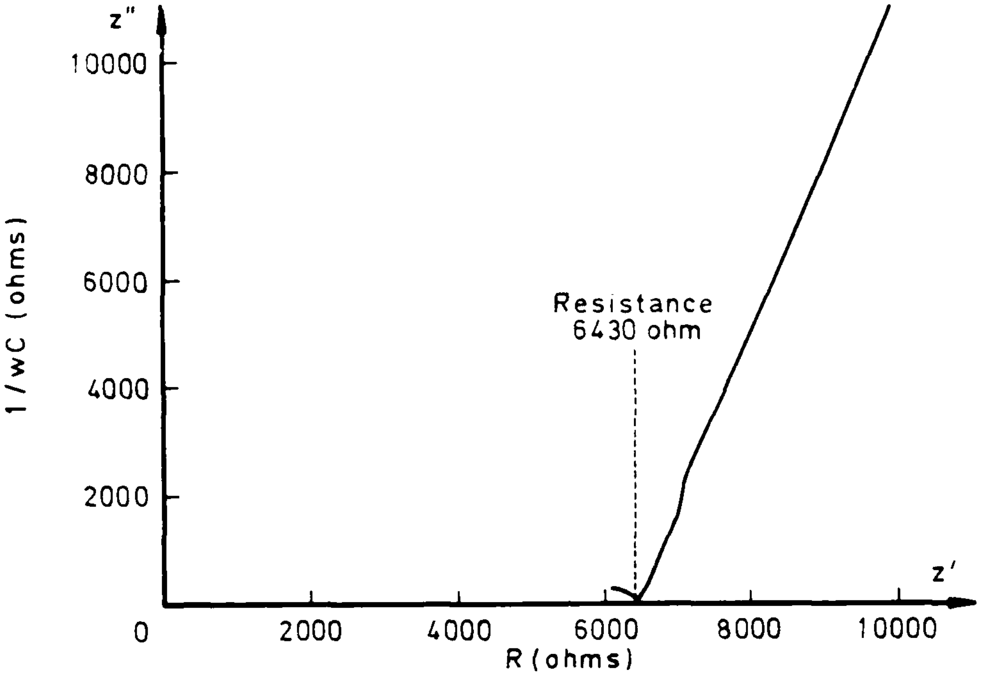


Fig 2 Impedance plot of 1:15 $LiC10_4$: polymer at 94°C

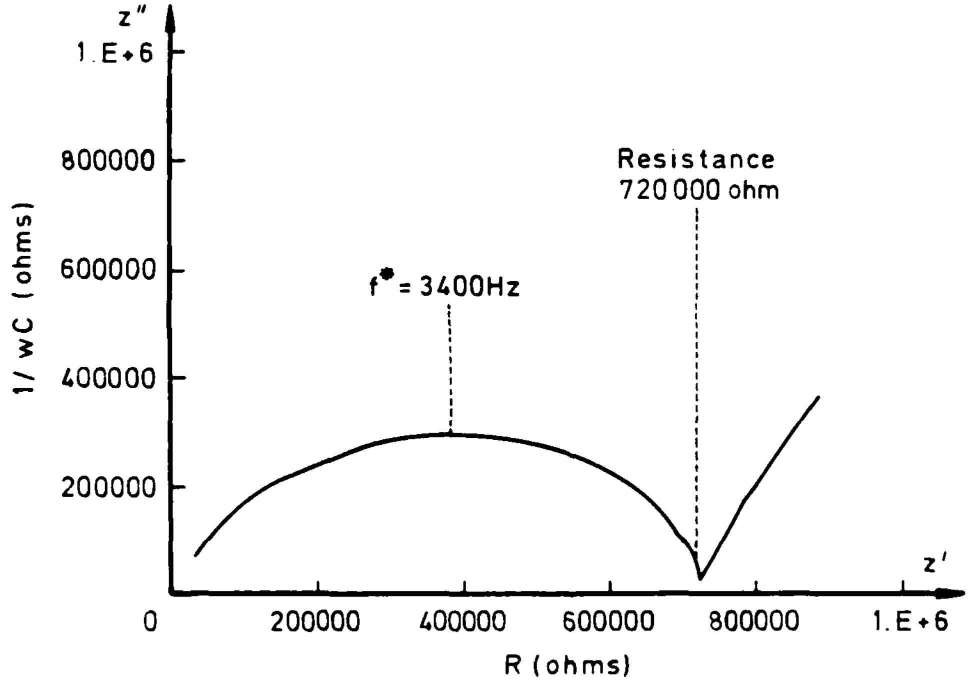


Fig 3 Impedance plot of 1:15 $LiC10_4$: polymer at 37.5°C

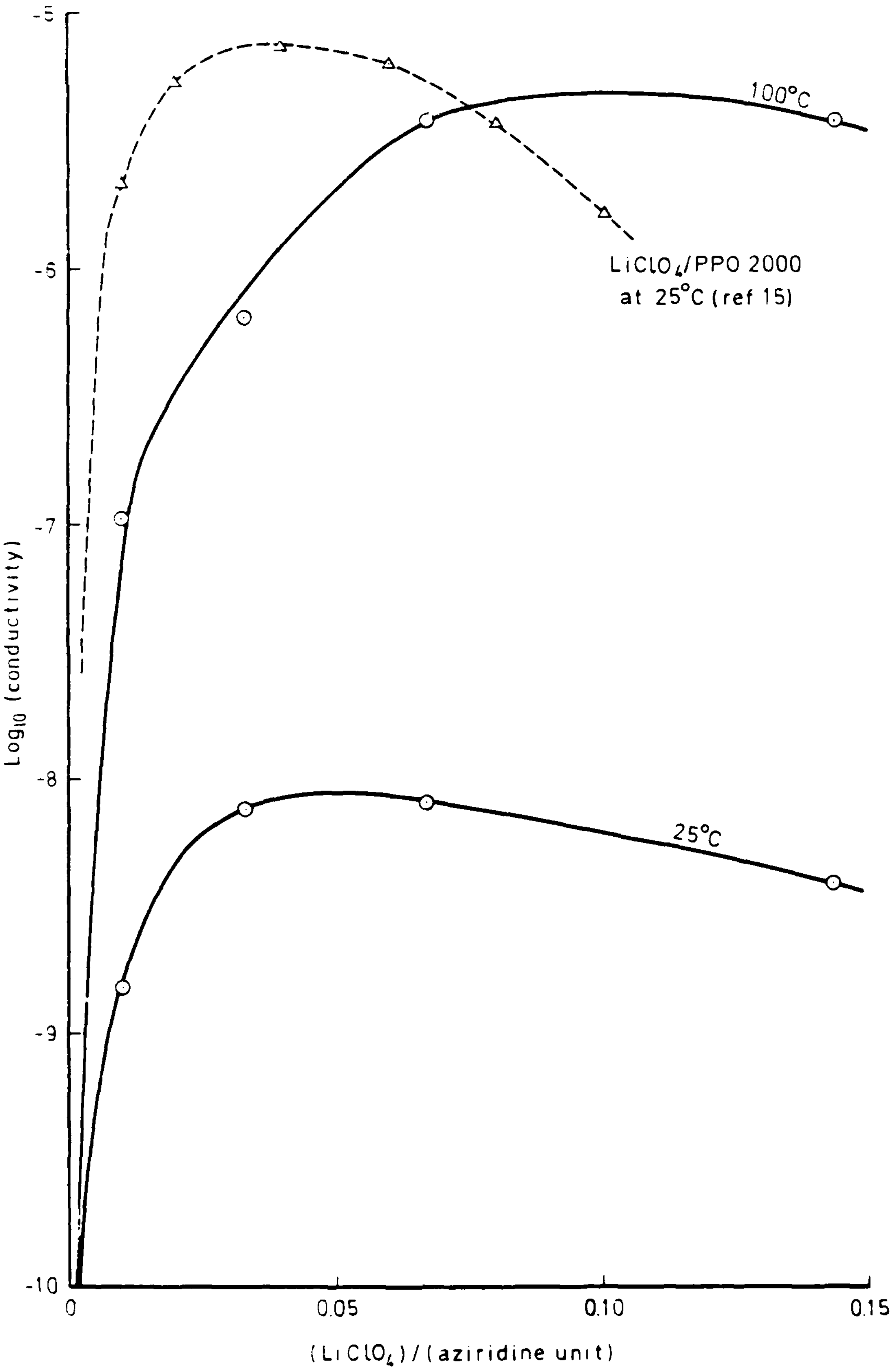


Fig 4 Effect of salt concentration on conductivity

Fig 5

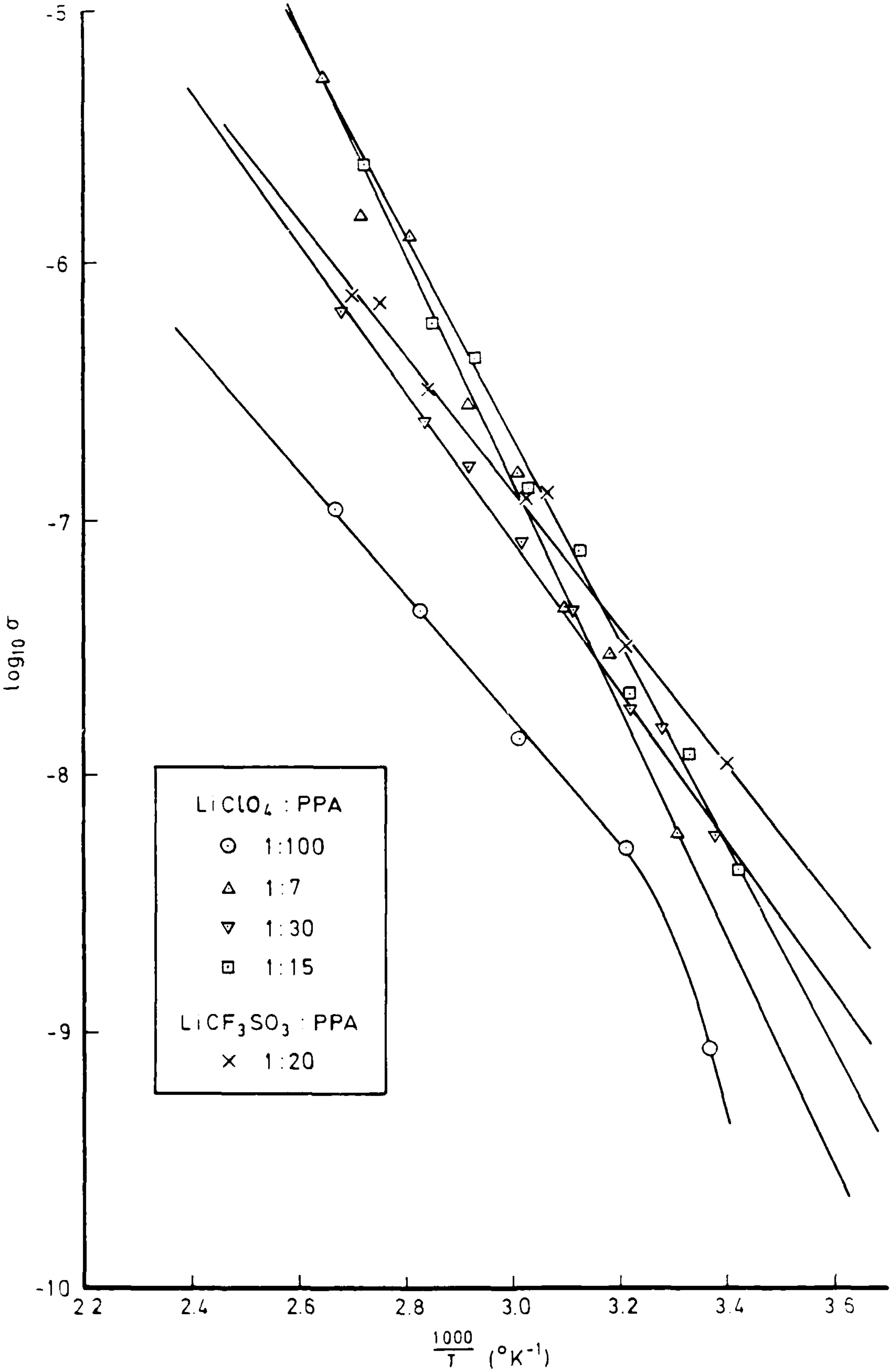


Fig 5 Arrhenius conductivity — temperature plots for polymer/salt compositions

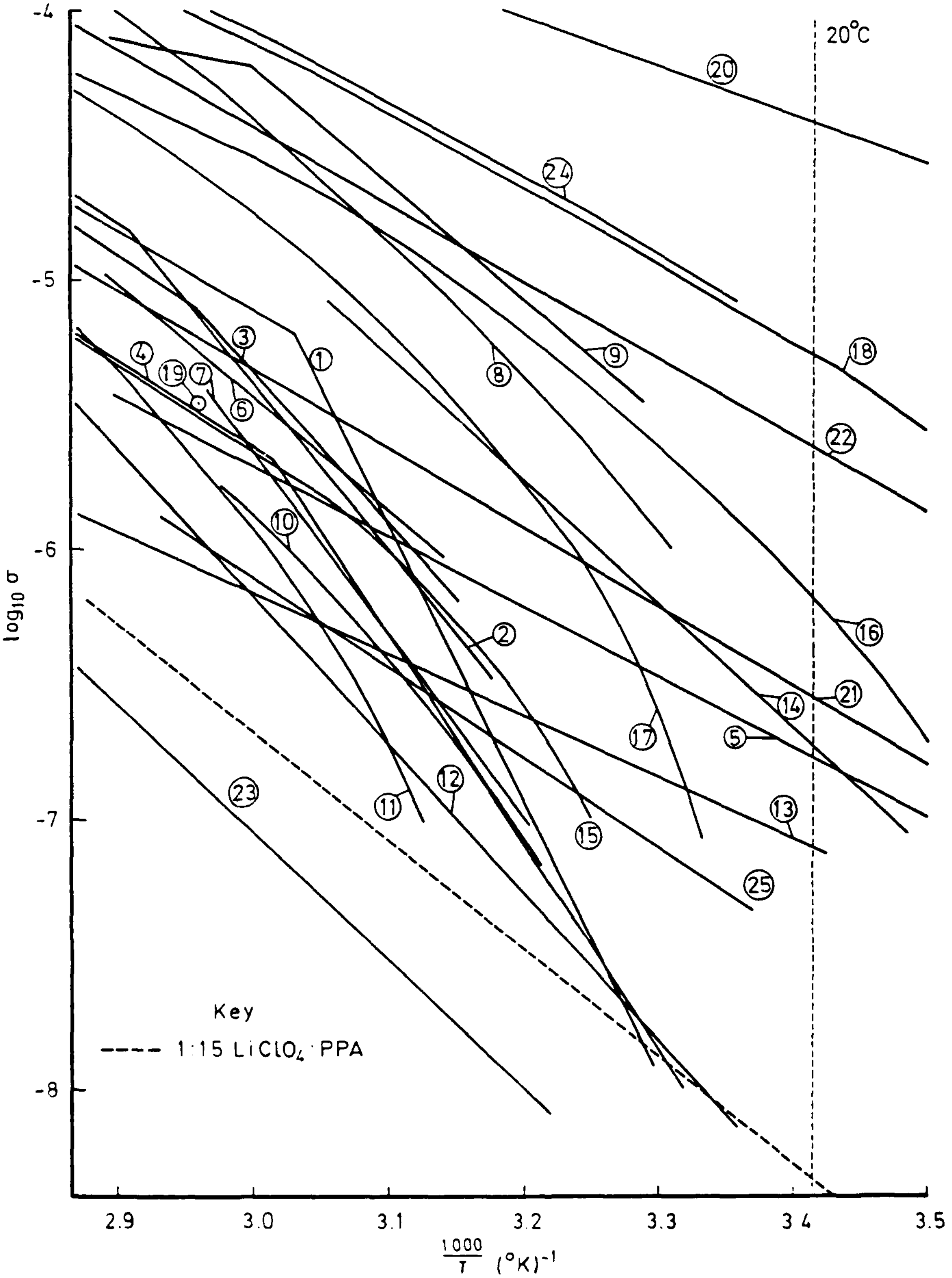


Fig 6 Comparison of conductivity – temperature plots for various electrolytes

CAPTIONS FOR FIGURE 6

No.	Composition	Reference
1	$(PEO)_8LiCF_3SO_3$	Solid State Ionics, 11, (1), 91 (1983) [Armand]
2	$(PEO)_{10.4}LiCF_3SO_3$	Solid State Ionics, 2, 347 (1981) [Steele]
3	$(PEO)_{8.1}LiCF_3SO_3$	Solid State Ionics, 2, 347 (1981) [Steele]
4	$(PEO)_6LiCF_3SO_3$	Solid State Ionics, 2, 347 (1981) [Steele]
5	$(PEO)_{4.5}LiCF_3SO_3$	Polymer, 23, 690 (1982) [Wright]
6	$(PEO)_8LiClO_4$, 'low-purity'	Solid State Ionics, 2, 347 (1981) [Steele]
7	$(PEO)_{8.2}LiClO_4$	Solid State Ionics, 2, 347 (1981) [Steele]
8	$(PEO)_8LiClO_4$, 'high-purity'	Solid State Ionics, 7, 61 (1982) [Steele]
9	$(PEO)_8LiClO_4$	Solid State Ionics Conference, Grenoble, July 1983 [Fontanella]
10	$(PEO)_5LiSCN$	Solid State Ionics Conference, Grenoble, July 1983 [Fontanella]
11	$(PEO)_5LiSCN$	"Fast Ion Transport in Solids", Ed. Vashishta, Mundy, Shenoy; North Holland p 131 (1979) [Armand]
12	$(PEO)_{4.5}LiSCN$	Electrochim. Acta., 27, (12), 1671 (1982) [Sorensen]
13	$(PEO)_4LiBF_4$	Polymer, 23, 690 (1982) [Wright]
14	$(PEO)_5LiCF_3CO_2$	Solid State Ionics, 5, 681 (1981) [Tanzella]
15	$(PPO)_{12}LiCF_3SO_3$	Proc. Lithium Nonaqueous Battery Electrochemistry Conference, Cleveland (1980) [Armand]
16	$(PPO)_9LiCF_3SO_3$	Proc. Lithium Nonaqueous Battery Electrochemistry Conference, Cleveland (1980) [Armand]
17	$(PPO)_6LiCF_3SO_3$	Proc. Lithium Nonaqueous Battery Electrochemistry Conference, Cleveland (1980) [Armand]
18	$(PPO)_{25}LiClO_4$	Polymer, J., 15, (2), 175 (1983) [Watanabe]
19	[poly(ethylene succinate)]$_3LiBF_4$	Solid State Ionics Conference, Grenoble, July 1983 [Shriver]
20	67% poly(acrylonitrile) 7% $LiClO_4$ 26% ethylene carbonate	J. Poly. Sci., (Poly. Phys. Ed.), 21, 939 (1983) [Watanabe]
21	70% poly(acrylonitrile) 18% $LiClO_4$ 11.5% ethylene carbonate	J. Poly. Sci., (Poly. Phys. Ed.), 21, 939 (1983) [Watanabe]
22	50% poly(vinylidene fluoride) 21% $LiClO_4$ 29% propylene carbonate	Electrochim. Acta., 28, (5), 591 (1983) [Tsuchida]
23	8% $LiClO_4$ in 1:1 PEG 400:triphenylmethyl-tri-isocyanate	Poly. Bull., 6, 351 (1982) [Cheradame]
24	$LiBF_4$ in PEO 400 - maleate gel	Polymer, 23, 690 (1982) [Wright]
25	(PPO polycation)$_{25}LiClO_4$	Poly. J., 14, (11), 877 (1982) [Watanabe]