

POLYMER ELECTROLYTES*

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Summary

The ability of certain polymers to complex with a variety of salts and form electrolytes has been known for more than a decade. These polymer electrolytes can be manufactured in thin films with moderate conductivity, have a broad voltage stability window and form a deformable, stable interface with many electrode materials. As a result of these properties polymer electrolytes offer unique advantages in solid state batteries.

Several aspects of the preparation and performance of these electrolytes are discussed in this article.

Introduction

Until fairly recently battery research was directed towards improvement of existing cells rather than investigation of alternative systems. This situation was dramatically changed by advances in the semiconductor and microelectronics industry. The large scale production of integrated circuits and rapid increase in the number of battery powered devices available to the consumer had the effect of stimulating the battery industry to produce improved systems. Today a new generation of batteries,

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smaller, lighter and more powerful is replacing conventional cells in many applications.

One of the most active areas of battery research is that of ambient temperature lithium based cells. The high electrochemical potential of lithium coupled with its low density results in outstanding energy density. With the discovery in the mid sixties of the class of solid electrolytes, materials which allow the transport of ions through the electrolyte lattice, came the suggestion that their use in an all-solid-state cell would be advantageous. During the last decade the development of lithium ion conducting polymer electrolytes has brought this objective closer to reality.

The existence of ion-dipole interactions between polyethers and various salts, ^(1,2) and the fact that certain polymers facilitate the transport of ionic species, ⁽³⁾ was recognised several years ago. In 1973

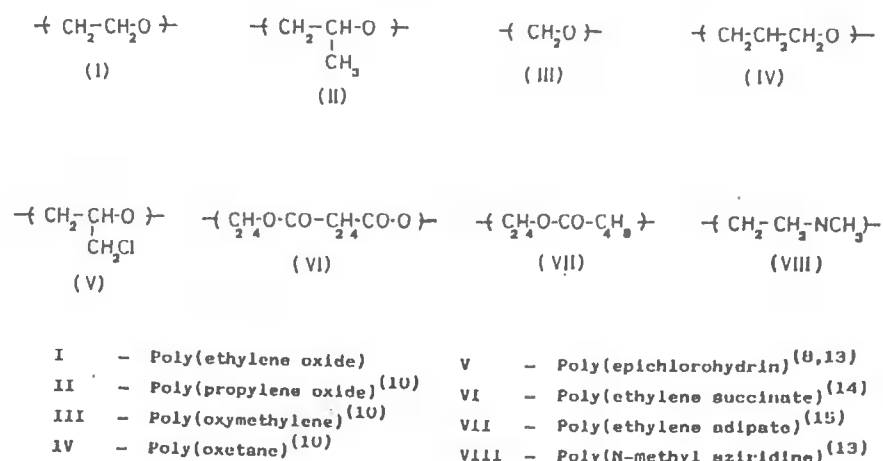


Figure 1 - Structural formulae of polymers

Fenton *et al* ⁽⁴⁾ reported the formation of high melting point crystalline complexes of poly(ethylene oxide) with several sodium and potassium salts. Subsequently the temperature dependence of ionic conduction in complexes of sodium, potassium, ammonium ^(5,6) and lithium salts ⁽⁷⁾ with poly(ethylene oxide), (see Figure 1 for structure), was described in greater detail.

The high conductivity of these polymers relative to vitreous and crystalline lithium ion conducting electrolytes and the suggestion that these polymers might form the basis of room temperature lithium batteries led to a rapid increase in the interest in this subset of solid electrolytes. Since these early results were published a large background of encouraging results has been added which confirms the viability of this proposal.

Polymer-salt complex formation

Polymer electrolytes may be prepared from many alkali metal salts and a variety of polymers. Several preparative methods have been successfully employed. An electrolyte may be prepared by extended exposure of a cast pure polymer film to a saturated solution of an appropriate salt in a solvent in which both the pure polymer and the complex are insoluble. This method, in theory, will lead to a stable polymer in which the complex has the maximum salt content.

Alternatively, an appropriate weight of the salt may be directly dissolved in a known weight of molten polymer. Different polymers show different solubility for added salts and in early research in this field it was this solubility which determined the ratio of salt used to produce the polymer electrolyte.

By far the most commonly used preparative method involves the dissolution of known weights of polymer and salt in a suitable solvent. The mixture is stirred until homogeneous and then cast onto a plate of glass or teflon, or into formers, depending on the required film thickness. Finally the solvent is removed from the polymer film by slow evaporation, by vacuum treatment, or by vacuum and heat treatment.

Table 1 - Comparison of poly(ethylene oxide) - salt complex formation with lattice energies of the pure salts (8)

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	No 1 036	No 923	No 821	No 785	No 740
Cl ⁻	Yes 853	No 786	No 715	No 689	No 659
CH ₃ CO ⁻ ₂	- 881	No 763	- 682	- 656	- 682
NO ⁻ ₃	- 846	No 756	- 687	- 658	No 625
NO ⁻ ₂	- -	No 748	- 664	- 765	- 598
Br ⁻	Yes 807	Yes 747	No 682	No 660	No 631
N ⁻ ₃	- 818	No 731	- 658	- 632	- 604
BH ⁻ ₄	- 778	Yes 703	- 665	- 648	- 628
I ⁻	Yes 757	Yes 704	- 644	No 630	No 604
SCN ⁻	Yes 807	Yes 682	Yes 616	Yes 619	Yes 568
ClO ⁻ ₄	Yes 723	Yes 648	- 602	- 582	- 542
CF ₃ SO ₃	Yes 725	Yes 650	Yes 605	Yes 585	Yes 550
BF ⁻ ₄	Yes 699	Yes 619	- 631	- 605	- 556
BPh ⁻ ₄	Yes 700	Yes 630	Yes 630	Yes 600	Yes 550

No = no solvent free complex formed;
Yes = solvent free complex formed.

The polymer product is usually described by the use of ratios of monomer unit to inorganic salt, for example PEO₈ LiClO₄ indicates that there are 8 monomer units to each lithium perchlorate unit in the electrolyte. The use of the abbreviation PEO instead of EO to indicate the monomer unit is confusing in this nomenclature and it has recently been suggested that this electrolyte is described as EO₈ LiClO₄ or alternatively referred to as having a lithium ion to ethylene oxide repeat unit ratio of 1:8.

As reference to Table 1 demonstrates there are many salts which form complexes with poly(ethylene oxide). In most cases these salts contain large anions and therefore have fairly low lattice energies. Shriver *et al* (8) have shown that for each cation of the alkali metal series there is a threshold value of lattice energies above which complex formation does not occur.

So far only poly(ethylene oxide) based electrolytes have been considered, however it has been demonstrated that many polymers can be used to produce electrolytes by combination with salts.

Shriver *et al* (8,9) listed three attributes which might be expected to be conducive to complex formation

1. The polymer should have a high concentration of polar groups which can effectively solvate the cation and/or anion of the added salt,
 2. The polymer backbone should be highly flexible to permit polymer reorganisation and cation solvation,
- and
3. In general the polymer should have a low cohesive energy density to produce a favourable free energy change upon polymer-salt interaction.

Attempts to improve on the performance of poly(ethylene oxide) led to investigation of polymers with similar structural features. Armand (10) demonstrated that poly(propylene oxide), (Figure 1, II), was also capable of forming conducting complexes. The polymer used by Armand was non-stereoregular, with a low degree of crystallinity. Table 2 summarises the results reported for these systems. A reduction in the solvating properties of this polymer, relative to poly(ethylene oxide), was explained in terms of

Table 2 - Electrolyte behaviour of poly(propylene oxide) based systems (10).

- + existence of a complex
- non-existence

a b° a stoichiometry, expressed as the O to M⁺ ratio
 b temperature, in degrees Centigrade, at which the conductivity of the electrolyte exceeds 10⁻⁵ (Ω cm)⁻¹

anions	cations	Li ⁺		Na ⁺	
		a	b°	a	b°
Br ⁻		6	135°	-	
		10	150°		
I ⁻		8	65°	-	
B(C ₆ H ₅) ₄ ⁻		+		10	80°
CF ₃ SO ₃ ⁻		6	85°	6	85°
		9	55°	8	55°
		12	60°	10	50°
				12	45°
				14	45°
				16	45°
ClO ₄ ⁻		+		+	

steric hindrance. Apparently the increased donicity of the oxygen atom, now adjacent to a secondary, rather than primary carbon, does not compensate for the steric factor. It is interesting to note that other members of the polyolefinic oxide series, poly(oxymethylene), (Figure 1, III), and poly(oxetane), (Figure 1, IV), are not complex forming (10), presumably as a consequence of the distance between successive oxygen atoms, which in poly(ethylene oxide) seems to be optimal.

Two different approaches have been reported for crosslinking poly(ethylene oxide), based on chemical additives (11) and sample irradiation (12). The crosslinked polymer produced by irradiation showed enhanced conductivity at close to ambient temperatures.

Samples of atactic poly(epichlorohydrin), (Figure 1, V), were assessed by Shriver et al (8) and Armand (13) but results appear to confirm that steric hindrance at the oxygen site in the polymer reduces the complexation efficiency of this macromolecule.

Poly(ethylene succinate), (Figure 1, VI), also investigated by Shriver (14) was found to complex with Li BF₄, Li CF₃CO₂, Li CF₃SO₃ and Na CF₃SO₃, but showed conductivities significantly less than the poly(ethylene oxide) Li ClO₄ electrolyte.

Poly(ethylene adipate), (Figure 1, VII), which has a structure similar to that of poly(ethylene succinate), has been reported by Armstrong (15) as a moderate electrolyte with Li CF₃SO₃.

In view of the favorable donor number of nitrogen one might predict that nitrogen analogues of poly(ethylene oxide) might be promising but unfortunately poly(N-methyl aziridine), (Figure 1, VIII), is difficult to prepare and the conductivity is disappointing (13). Once again it seems likely that the methyl sidegroup impedes the transport of the cation in the electrolyte.

The electrolytes mentioned in this section are intended only to illustrate the variety of polymers which are capable of complexing with added salts. These polymers represent a fraction of the numerous systems described in the literature.

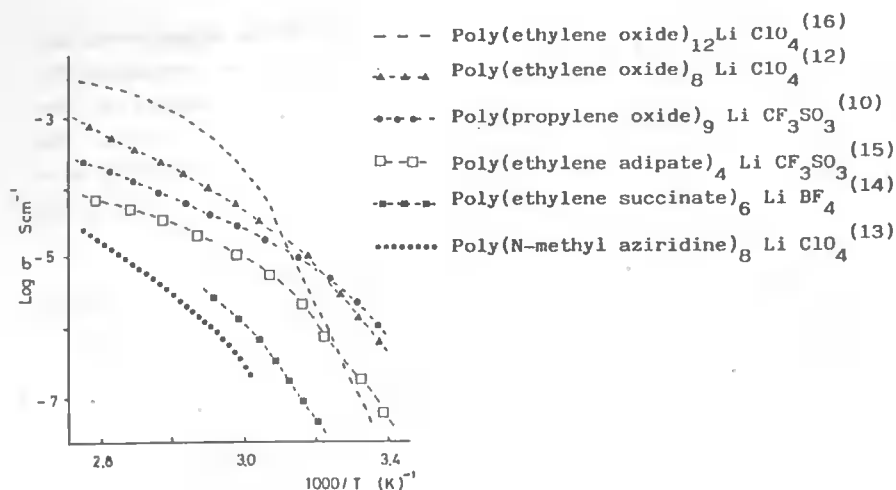


Figure 2 - Comparison of electrolyte conductivities

Figure 2 is included to show how the conductivity of some of the electrolytes described varies with temperature.

A separate class of polymer electrolytes not included in this review is formed by the ternary systems which have been described by Tsuchida and co-workers (17-21). These authors have investigated systems which contain lithium salts, polymers and solvents, usually dimethyl formamide, γ -butyrolactone, propylene carbonate or ethylene carbonate.

The gels which are formed by these mixtures have appreciable conductivities, and do not suffer from the practical disadvantage of liquid electrolytes with respect to leakage. As far as ion transport is concerned however they offer no advantage over polymer electrolytes, their voltage stability window is closely related to that of the solvent and they are restricted to near-room temperature operation by the solvent volatility. The type of ion conduction involved differs from that observed in binary polymer electrolytes and thus this group of electrolytes will not be discussed further in this review.

The evolution of the ion transport mechanism.

While ionic conductivity is an important property to be taken into consideration when evaluating an electrolyte for battery applications, there are other features which are almost as crucial. Among these are the cationic transport number and the compatibility of the electrolyte with electrode materials. Particular attention has been directed toward the elucidation of the ion transport mechanism in the hope that a more complete understanding of the process may lead to electrolytes with improved conductivity and transport properties.

The earliest conductivity measurements on polyolefinic polymers were carried out in 1968 by Binks and Sharples (3). These authors observed a considerably higher degree of conductivity in pure poly(ethylene oxide) than other saturated polymers and suggested that the conduction mechanism involved a "handing-on" mechanism based on the transport of protons through local segmental motion of the polymer chains. Poly(ethylene oxide), in common with many other highly stereoregular polymers, favours a high degree of crystallinity. The polymer structure is a mixture of amorphous and crystalline regions. The mechanism proposed by Binks and Sharples involved proton removal from the polymer chain and transfer to an ether oxygen on a neighbouring amorphous chain segment. In 1966 Lundberg *et al* (2) reported the results of stiffness modulus experiments which showed that the addition of inorganic salts to polyethylene oxide caused a decrease in the crystallinity of polymers.

Reasoning that a decrease in poly(ethylene oxide) crystallinity should result in enhanced conduction, Wright (5,6) investigated the conductivity of poly(ethylene oxide) K SCN electrolytes. The results of these experiments were interpreted by Wright as indicating that the conduction process was controlled by the contortions of free polymer chains in the amorphous regions of the electrolyte structure. Figure 3 is included to show the polymer segment conformation which Wright suggested might lead to cation transfer. Wright however did not exclude the possibility that a significant contribution to conduction occurred in the crystalline regions of the electrolyte. Investigating the temperature dependence of electrical conductivity, Wright found a transition from a high to low activation energy

process coincided with the crystalline melting point of the poly(ethylene oxide). He interpreted this observation in terms of thermal disintegration of local structure allowing more facile displacement of polymer chain segments.



Figure 3 - Polymer segment conformation leading to cation transport (5)

Between 1978 and 1979 results obtained with various electrolytes led Armand et al (7,10) to suggest an alternative model of conduction in polymer electrolytes. X-ray structural studies of pure poly(ethylene oxide) (22) and complexes of the polymer with inorganic salts (23,24) have shown that both the pure polymer and the complexes have helical structures. In the complexes with inorganic salts the cations reside within the helical structure of the polymer. The proportion of salt to poly(ethylene oxide) repeat unit in the complexes studied was found to be 4 to 1. The model Armand proposed involved the formation of a regular helix filled by the cations, M^+ , which were solvated by 4 ether oxygens in the polymer chain. The counterions, X^- , were situated outside the helix. The structural parameters of the complex, and the interaction energies are determined by the size of the coordinating cation. At high temperature the structure of the complex tends toward disorganisation with vacancies in the complex structure being created, (Figure 4). Armand suggested that the type of transformation and consequent changes in electrolyte conductivity were dependent on the cation size.

In spite of their simple structure the behaviour of poly(ethylene oxide) -salt complexes is relatively complicated because it is influenced by

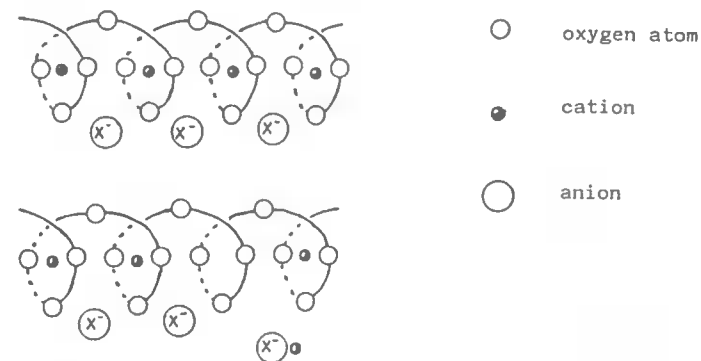


Figure 4 - Vacancy mechanism for cation transport (7)

the crystallinity of the electrolyte sample. Where polymers are concerned the definition of crystalline or amorphous is not straightforward. Structural studies of polymers are generally conducted on drawn fibres of polymers to obtain a highly crystalline sample, but the macroscopic structure of electrolytes is more realistically, viewed as being composed of a complex mixture of crystalline and amorphous regions. Since amorphous fields separate crystalline regions of a heterogeneous polymer electrolyte the mobile species must be able to move through both phases if d.c. conductivity is to be accounted for. In cast polymer electrolyte films a continuous range of crystallinity can exist and as the percentage crystallinity of the electrolyte increases the conductivity of the polymers generally changes to a different form. These changes in the conductivity mechanism are often reflected in the type of conductivity-temperature behaviour which polymer electrolytes show, (Figure 5). The results obtained by Armand for electrolytes based on poly(ethylene oxide) with potassium, sodium and lithium thiocyanates as added salts demonstrate how apparently similar salts can give rise to remarkably different conductivity behaviour.

Using the following relation, and plotting $\ln \sigma$ versus $1/(T-T_0)$, Armand showed that curved $\ln \sigma$ versus $1/T$ plots could be linearised.

Armand interpreted the curved $\ln \sigma$ versus $1/T$ plots in terms of the free volume model with the introduction of the notion of continuously

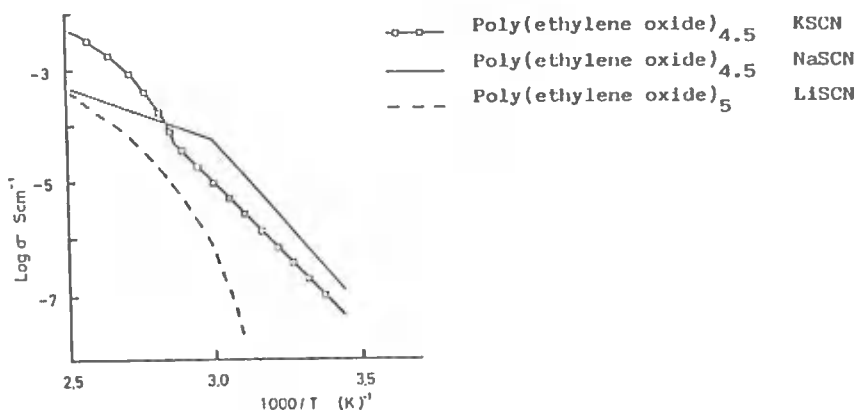


Figure 5 - Types of conductivity behaviour reported (10)

$$\sigma = AT^{1/2} \exp\left(\frac{E_a}{T-T_0}\right)$$

increasing disorder. T_0 in this equation represents the zero configurational entropy temperature, which in practice is normally fairly close to the glass transition temperature, T_g . Figure 6 is included to illustrate the effectiveness of this model in data linearisation, where $\ln \sigma T$ is plotted against $1/(T-T_0)$.

Based on these ideas Armand (10) classified the polymer electrolytes into three groups:

- Type I** electrolytes, which obey a free volume law (Vogel - Tamman - Fulcher), over the entire range of temperature investigated,
- Type II** electrolytes, which change from a linear Arrhenius type behaviour to a free volume relationship above a certain temperature and

Type III electrolytes, which show linear Arrhenius behaviour over the entire temperature range, generally with a change of gradient

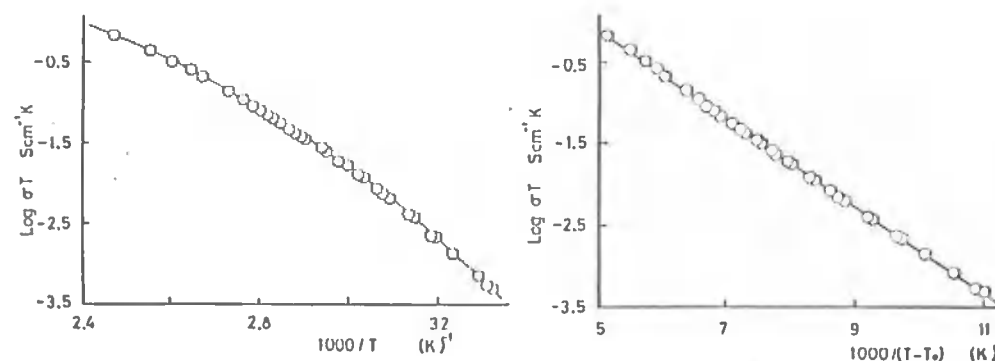


Figure 6 - Data linearisation for (ethylene oxide)₈ Li ClO₄ electrolyte (12)

In 1981 Steel *et al* (25) demonstrated that Armand's classification of electrolytes failed to place a series of electrolyte complexes based on the poly(ethylene oxide)-Li CF₃SO₃ system. Differential Scanning Calorimetry analysis of these electrolytes revealed the existence of two endothermic events on heating the sample from room temperature to 200°C, indicating that there were two distinct crystalline phases in the electrolytes. The first of these phases melted at about 60°C, close to the melting point of pure poly(ethylene oxide) polymer. Steele proposed that this phase contained very little or no lithium salt. On continued heating a gradual melting/dissolution of the other phase occurred at temperatures between 98 and 172°C, depending on the electrolyte composition. This phase was considered to be composed of the complex between the inorganic salt and the polymer. Having established that the electrolyte was largely amorphous above 60°C Steele investigated the form of the $\ln \sigma$ conductivity versus $1/T$ behaviour and found that a linear relationship was obtained, contradicting Armand's scheme of classification. These authors concluded that a free volume law might be applicable to the poly(ethylene oxide)-LiCF₃SO₃ electrolytes but that the range of temperatures

over which the measurements were made was not sufficient to allow this type of behaviour to be distinguished from true Arrhenius behaviour.

Subsequently Steele (26) confirmed that the preparation method of the electrolyte also influenced the form of the conductivity behaviour. Electrolytes with the composition $(\text{ethylene oxide})_8\text{LiClO}_4$ were prepared using acetonitrile of high and low purity as solvent to cast the polymer films.

These investigations showed that the form of the conductivity behaviour was dependent on the solvent purity, in one case a linear Arrhenius type relation was obtained, and in the other non-linear behaviour, Figure 7, was observed. Differences were also observed in the DSC behaviour, and interpreted in terms of the crystallisation rate of the polymer prepared from pure solvent being different from the other cast polymer. Steele concluded that the purity of the solvent used and conditions of electrolyte preparation have a dramatic effect on the percentage of amorphous polymer present and therefore on the conductivity of the electrolyte.

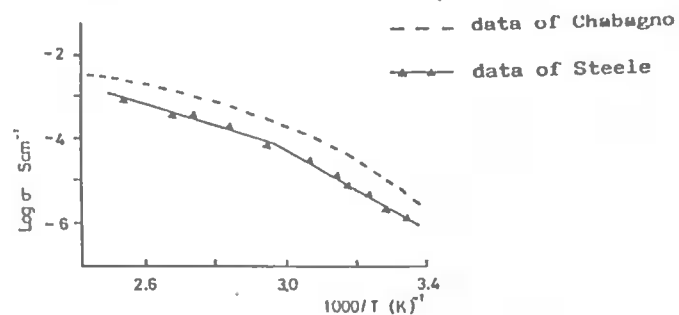


Figure 7 - Linear (26) and non-linear (16) behaviour with $(\text{ethylene oxide})_8\text{LiClO}_4$ electrolyte

Sorensen and Jacobsen (27) extended the results obtained by Steele et al, assuming that the crystalline electrolyte complex was a much poorer ionic conductor than the amorphous phase. They obtained an algebraic expression which related the conductivity and the amount of salt present. This expression was used to calculate the variation of the conductivity with the salt

concentration. Figure 8 shows the theoretical and experimental results obtained by Sorensen and Jacobsen for the $(\text{ethylene oxide})_x\text{LiCF}_3\text{SO}_3$ system.

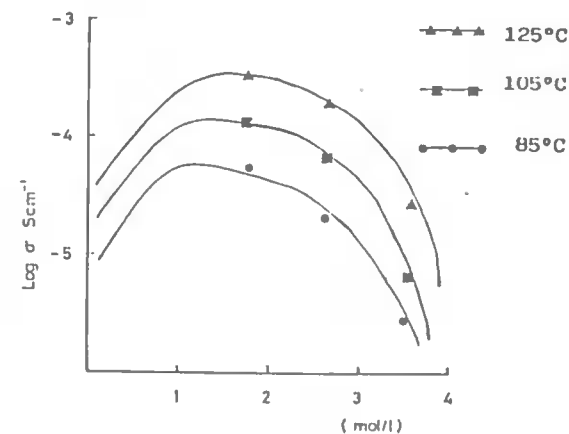


Figure 8 - Experimental (symbols) and calculated (lines) values for poly(ethylene oxide) LiCF_3SO_3 electrolytes (27)

Within a relatively short period these results were supported by evidence from the effect of pressure on the conductivity (28,29) and dielectric conductivity spectra (30) which confirmed that the concept of conduction occurring by ion-hopping in the helical crystalline complex, was now unacceptable.

Conclusive evidence from NMR measurements confirms that even in

apparently largely crystalline materials the conduction process is based on segmental motion of the polymer chain. Armand et al ⁽³¹⁾ used the transverse nuclear magnetisation correlation function to estimate the temperature dependence of the fraction of protons belonging to the crystalline phase of the electrolyte. These workers confirmed that in (ethylene oxide)₈ Li CF₃ SO₃ at 20°C approximately 90% of the protons of the polyethylene oxide molecules are in the crystalline phase. As the electrolyte sample is heated this proportion decreases to about 35% at close to 50°C. On further heating this percentage is reduced to 0% at 150°C, (Figure 9). The same procedure was applied to determine the fraction of the salt which was associated with the crystalline phase. In this case the results indicated that the salt remained mostly in the crystalline phase until about 70°C when slow dissolution into the amorphous phase began. Armand interpreted these results as indicating that the sharp drop in crystallinity at between 30 and 50°C was due entirely to the melting/dissolution of uncomplexed polyethylene oxide and thus the crystalline phase left above this temperature is the salt rich complex of poly(ethylene oxide). This complex is progressively dissolved into the amorphous material as the temperature is increased between 50 and 150°C.

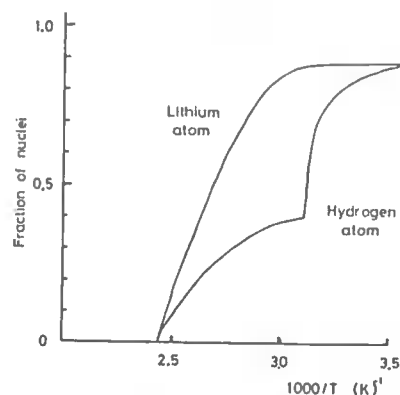


Figure 9 - Variation of fraction of nuclei in the crystalline phase with temperature for poly(ethylene oxide) Li CF₃SO₃ electrolytes ⁽³¹⁾

The results obtained in these experiments confirm that the form of

the conductivity versus temperature behaviour is a complex function of several factors giving rise to the variety of behaviour observed for different electrolytes. It was also established by the absence of motional narrowing of the ⁷Li and ¹⁹F resonance lines that neither cations nor anions are mobile in the salt rich complex, confirming the supposition made by Sorensen et al ⁽²⁷⁾ in their analysis.

We have seen in this section how the model of the ion transport process in polymer electrolytes changed in the few years after their discovery. During this period the accepted value of the cation transport number also changed. Early attempts to measure this quantity reported values close to unity ⁽⁷⁾, a value which seemed consistent with an ion-hopping mechanism in a helical polymer complex. Emf measurements ^(16,32) confirmed that the electronic conductivity of the electrolyte was low. In 1982 Sorensen and Jacobsen ⁽³³⁾ reported results of a.c. impedance experiments on the poly(ethylene oxide)-Li SCN electrolyte with lithium electrodes using the Macdonald analysis to estimate the cationic transport number. The values they reported were between 0.51 and 0.58. These results were supported by radiotracer diffusion ⁽²⁹⁾ experiments, a modified Tubandt method ^(34,35) for estimating the transport number, and evidence from the effect of pressure ⁽²⁸⁾ on the conductivity of poly(ethylene oxide) based electrolytes.

The conflict between values for the cation transport led to attention being diverted to this problem. Armand ⁽¹¹⁾ criticised the application of the Macdonald analysis to the polymer case on the grounds that the model requires an ideal solution behaviour in the whole concentration range, a condition not met because of total immobility of both species in the crystalline complex phase. Sorensen and Jacobsen ⁽³⁶⁾ reported the results of chronoamperometric experiments and further complex impedance experiments. Unfortunately these methods produced very different values of t^+ and though it is now accepted that the anion is mobile in polymer electrolytes no method has been reported which gives reliable values for the anion transport number.

The importance of the transport number of electrolytes for use in cells lies in the consequence of development of concentration profiles of the mobile species at the electrodes. These will impose a limiting current on the cell and may result in the formation of non-conducting crystalline complex zones in the electrolyte. The problem of the transport number in polymer

electrolytes remains an important and controversial issue.

Applications of polymer electrolytes

Solid electrolytes have been used in applications as diverse as coulometers, timers, and electrochemical detectors ⁽³⁷⁾ and recently a polymer electrolyte has been applied in a photovoltaic device ⁽³⁸⁾, however without doubt the most important application has been in energy storage in primary and secondary cells.

In general, the lithium ion conductivity in solid electrolytes is lower than in aprotic organic electrolytes, such as propylene carbonate or dimethoxyethane, containing lithium salts. Cells containing liquid electrolytes however are susceptible to leakage and as the solvents used are often inflammable their use constitutes a hazard, particularly when lithium metal is present as anode. Several inorganic crystalline and vitreous solids have been considered for applications in lithium cells but their relatively low conductivity requires the production of thin films of electrolytes with large surface areas to achieve even moderate current densities. Since the development of poly(ethylene oxide) based electrolytes, which combine the advantages of flexibility, ease of fabrication in thin films with large surface areas, moderate conductivities at temperatures slightly above ambient and excellent electrode/electrolyte interface stability ^(13,39-41), several programs ⁽⁴²⁻⁴⁵⁾ of advanced battery development have been based on polymer systems. Preliminary investigations have been directed toward fabrication and characterisation of cells using composite cathodes of V_6O_{13} ⁽⁴²⁾ and TiS_2 ⁽⁴⁵⁾ and lithium metal anodes at operating temperatures between 100 and 140°C. These cathode materials are examples of "solid solution electrodes", compounds which are able to reversibly incorporate guest species in their crystal structure and are therefore suitable electrodes for secondary cells. Figure 10 shows the cell design used by Hooper ⁽⁴²⁾ and Figures 11 and 12 show the results obtained by Hooper and Armand ⁽⁴⁵⁾ with $Li_xV_6O_{13}$ and Li_xTiS_2 anodes respectively. Some difficulties were encountered with the V_6O_{13} cathode materials where cell assembly methods gave rise to inhomogeneous distribution of the active electrode material with a consequential reduction in the

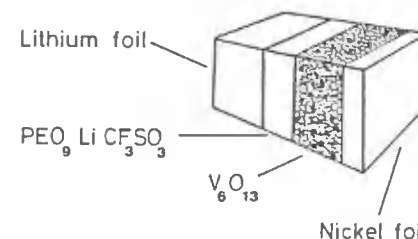


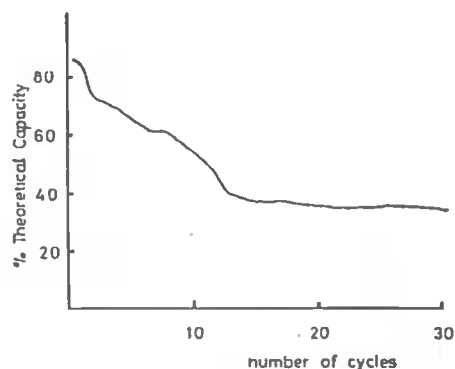
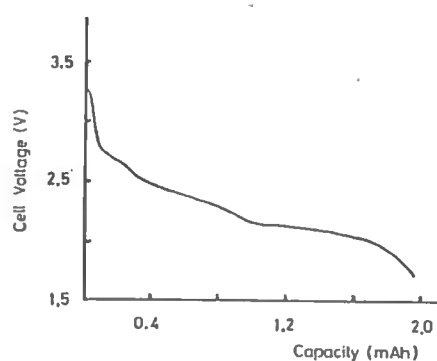
Figure 10 - Design of V_6O_{13} based all-solid-state cell ⁽⁴²⁾

utilisation of the cathode. This problem was effectively resolved however by modification of the cell assembly procedure.

Both groups reported excellent cycling performance with little degradation of the cell capacity (after an initial "settling - in" period) during many deep charge/discharge cycles. The initial results are also encouraging from the point of view of energy and power density in both systems and preliminary scaling-up experiments for V_6O_{13} to electrode areas of 100-140cm² have not revealed any complications. It is interesting to compare the results of a recent assessment study, based on the V_6O_{13} cell, with conventional and other advanced systems. (Table 3). The value given for the

Table 3 - Comparison of Energy Densities

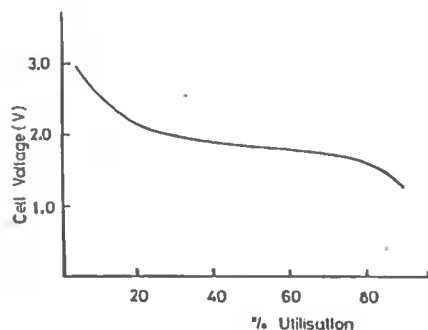
System	Energy Density (Wh. kg ⁻¹)
Li - V_6O_{13}	400 ⁽⁴²⁾
Li - TiS_2	100 ⁽⁴⁵⁾
Pb - PbO	30 - 40
Cd - NiO	15 - 37



Area 0.75 cm^2
 Temperature 104°C
 Theoretical capacity 2mAh

(42)

Figure 11 - Results obtained with the V_6O_{13} based cell



Area 3.8 cm^2
 Temperature 100°C
 Theoretical capacity 3.3mAh
 Current density $0.5\text{mA}/\text{cm}^2$

(45)

Figure 12 - Results obtained with the TiS_2 based cell

energy density for the V_6O_{13} system apparently includes realistic estimates for the contribution of cell cases, busbars and terminals, and thermal management systems. Although the results obtained using poly(ethylene oxide) based electrolytes are already very impressive a further improvement in the electrolyte conductivity would allow cell operation at lower temperatures or higher current densities. Research continues in many laboratories with this goal.

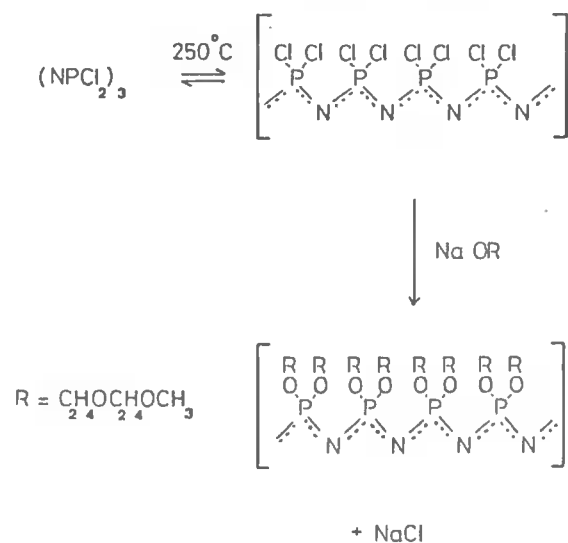
Directions of future research

The result of initial interest in polymer electrolytes was a rapid evaluation of commercially available polymers as possible electrolytes. Some of the more promising polymers have been discussed in the experimental section however it became obvious fairly rapidly that no commercially available polymer could be used to prepare electrolytes with conductivities as high as the poly(ethylene oxide) based electrolytes. Attempts to improve on the performance of poly(ethylene oxide) have subsequently involved either synthesis of novel polymers or modification of commercial polymers to achieve poly(ethylene oxide)-like structures with improved conductivity. These two approaches are illustrated with two examples.

From the viewpoint of conductivity the most attractive electrolyte reported so far is based on the very flexible polyphosphazene backbone (46,47).

Sidechains designed to mimic the structure of poly(ethylene oxide) chains, 2-(2-methoxy ethoxy) ethanol, were grafted onto the polymer as shown in Scheme 1. In this case the relatively high glass transition temperature means the polymer is an elastomer at room temperature. Figure 13 is included to allow comparison of this electrolyte with the (ethylene oxide)₁₂ LiClO_4 system.

Various attempts at improving mechanical properties of polymers electrolytes have been reported (12,48-51) however a novel and fruitful approach has been investigated by Vincent and coworkers (52). One of the difficulties encountered with poly(ethylene oxide) based electrolytes and elastomers such as polyphosphazene derivatives, is related to the tendency of



Scheme 1 2 - (2 - methoxyethoxy) ethanol substituted poly(phosphazene) synthesis (46,47)

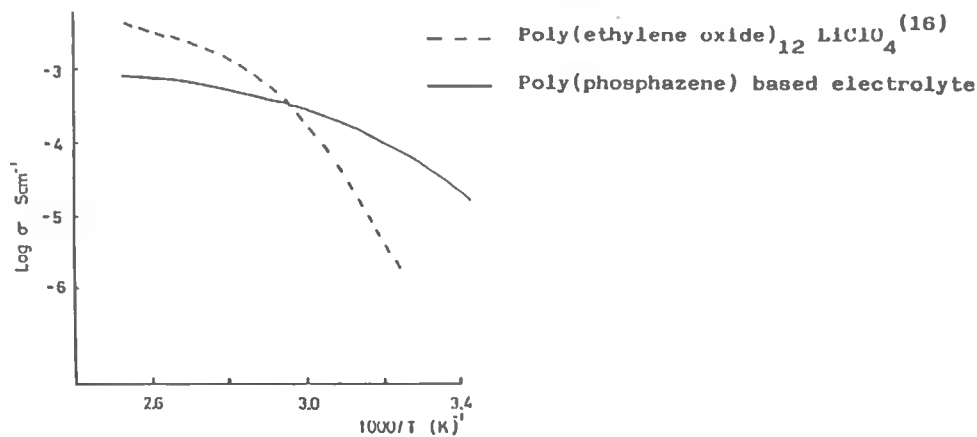


Figure 13 - Comparison of poly(phosphazene) based electrolyte with the (ethylene oxide)₁₂ Li ClO₄ system (46,47)

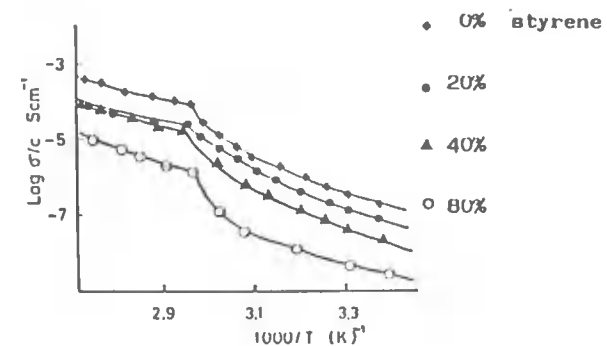


Figure 14 - Conductivity of Poly(ethylene oxide) - polystyrene based electrolytes (52)

these materials to creep under load at moderate temperatures. The solution to this problem proposed by Vincent and coworkers involved establishing a structural framework at a molecular level. Polystyrene, a polymer with a high glass transition temperature, ($T_g = 100^\circ\text{C}$), was chosen as the support system and was thermally polymerised in the presence of a (ethylene oxide)₁₀ Li CF₃ SO₃ electrolyte complex. The results reported in Figure 14 and Table 4, demonstrate that a significant improvement in the polymer mechanical properties were obtained at a relatively low cost in terms of electrolyte conductivity.

Table 4 - Variation of Normalised Penetration with Volume% of Styrene (52)

Vol% Styrene	Normalised Penetration
0	1
20	0.11
40	0.18
60	0.067
80	0.0089

Since 1979, when polymer electrolytes were first presented as materials of interest in battery development, a growing international research effort has resulted in an improvement of the understanding of the conduction process in these materials. It seems very probable that the inventiveness of the electrochemists, materials scientists and polymer chemists who have been attracted to this field will continue to improve the properties of polymer electrolytes.

Conclusion

In general if a product is to be adopted by a manufacturer, commercialised on a large scale and accepted by the consumer, it must perform better, be cheaper or safer than existing products. It is unlikely that cells using polymer electrolytes could be produced more cheaply than the current systems, (zinc-carbon, alkaline-manganese, and lead oxide systems for example), and in terms of safety they offer no particular advantage. If they are adopted therefore it will be on the merit of their performance. Cells using state-of-the-art polymeric electrolytes do not offer high rate capabilities at ambient temperatures, however they have advantages of high energy and power densities, ruggedness, variable geometry, low self-discharge rates (long shelf-life), and may be constructed using currently available techniques borrowed from other industries. An area in which polymer electrolytes may find application is that of secondary lithium cells. At present there are no all-solid-state secondary cells which are being commercialised and it seems quite possible that the improvements which the next few years will bring in electrolyte performance and the development of higher rate cathode materials will result in the appearance of a polymer electrolyte based cell in the battery market.

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REFERENCES

- (1) BLUMBERG, A.A., POLLOCK, S.S., HOEVE, C.A.J., *J. Polym. Sci.*, (A), Vol. 2, 2499, (1964).
- (2) LUNDBERG, R.D., BAILEY, F.E., CALLARD, R.W., *J. Polym. Sci.*, (A-1), Vol. 4, 1563, (1966).
- (3) BINKS, A.E., SHARPLES, A., *J. Polym. Sci.*, (A-2), Vol 6, 407, (1966).
- (4) FENTON, D.E., PARKER, J.M., WRIGHT, P.V., *Polymer*, Vol. 14, 589, (1973).
- (5) WRIGHT, P.V., *Br. Polym. J.*, Vol. 7, 319, (1975).
- (6) WRIGHT, P.V., *J. Polym. Sci.*, Vol 14, 1955, (1976).
- (7) ARMAND, M., CHABAGNO, J.M., DUCLOT, M., Second International Meeting on Solid Electrolytes, Extended Abstracts, St. Andrews, Scotland, (1978).
- (8) SHRIVER, D.F., PAPKE, B.L., RATNER, M.A., DUPON, R., WONG, T., BRODWIN, M., *Solid State Ionics*, Vol. 5, 83, (1981).
- (9) PAPKE, B.L., RATNER, M.A., SHRIVER, D.F., *J. Phys. Chem. Solids.*, Vol. 42, 493, (1981).
- (10) ARMAND, M., CHABAGNO, J.M., DUCLOT, M.J., "Fast Ion Transport in Solids", Elsevier, North Holland Inc., Vashishta, Mundy, Shenoy, (eds), (1979).
- (11) KILLIS, A., LE NEST, J.F., CHERADAME, H., GANDINI, A., *Makromol., Chem.*, Vol. 183, 2835, (1982).
- (12) MAC CALLUM, J.R., SMITH, M.J., VINCENT, C.A., *Solid State Ionics*, Vol. 11, 307, (1984).
- (13) ARMAND, M., *Solid State Ionics*, Vol. 9+10, 745, (1983).
- (14) DUPON, R., PAPKE, B.L., RATNER, M.A., SHRIVER, D.F., *J. Electrochem. Soc.*, Vol. 131-3, 586, (1984).
- (15) ARMSTRONG, R.D., CLARKE, M.D., *Electrochem. Acta.*, Vol. 29, 1443, (1984)
- (16) CHABAGNO, J.M., Thesis, University of Grenoble, (1980).
- (17) WATANABE, M., KANBA, M., MATSUDA, H., TSUNEMI, K., MIZOGUCHI, K., TSUCHIDA, E., SHINOHARA, I., *Makromol. Chem., Rapid Commun.*, Vol 2, 741, (1981).
- (18) OHNO, H., MATSUDA, H., MIZOGUCHI, K., TSUCHIDA, E., *Polymer Bulletin*, Vol. 7, 271, (1982).

- (19) TSUCHIDA, E., OHNO, H., TSUNEMI, K., *Electrochim. Acta.*, Vol. 28, 591, (1983).
- (20) TSUNEMI, K., OHNO, H., TSUCHIDA, E., *Electrochim. Acta.*, Vol. 28, 833, (1983).
- (21) TSUCHIDA, E., OHNO, H., TSUNEMI, K., KOBAYASHI, N., *Solid State Ionics*, Vol. 11, 227, (1983).
- (22) TAKAHASHI, Y., TADOKORO, H., *Macromolecules*, Vol. 6, 672, (1973).
- (23) IWAMOTO, R., SAITO, Y., ISHIHANA, H., TADOKORO, H., *J. Polym. Sci.*, (A-2), Vol. 6, 1509, (1968).
- (24) PARKER, J.M., WRIGHT, P.V., LEE, C.C., *Polymer*, Vol. 22, 1305, (1981).
- (25) STEELE, B.C.H., WESTON, J.E., *Solid State Ionics*, Vol. 2, 347, (1981).
- (26) STEELE, B.C.H., WESTON, J.E., *Solid State Ionics*, Vol. 7, 81, (1982).
- (27) SORENSEN, P.R., JACOBSEN, T., *Polymer Bulletin*, Vol. 9, 47, (1982).
- (28) FONTANELLA, J.J., WINTERSGILL, M.C., CALAME, J.P., PURSEL, F.P., FIGUEROA, D.R., ANDEEN, C.G., *Solid State Ionics*, Vol. 9+10, 1139, (1983).
- (29) CHADWICK, A.V., STRANGE, J.H., WORBOYS, M.R., *Solid State Ionics*, Vol. 9+10, 1155, (1983).
- (30) WONG, T., BRODWIN, M., PAPKE, B.L., SHRIVER, D.F., *Solid State Ionics*, Vol. 5, 689, (1981).
- (31) BERTHIER, C., GORECKI, W., MINIER, M., ARMAND, M.B., CHABAGNO, J.M., RIGAUD, P., *Solid State Ionics*, Vol. 11, 91, (1983).
- (32) DUPON, R., WHITMORE, D.H., SHRIVER, D.F., *J. Electrochem. Soc.*, Vol. 128, 715, (1981).
- (33) SORENSEN, P.R., JACOBSEN, T., *Electrochim. Acta.*, Vol. 27, 1671, (1982).
- (34) LEVEQUE, M., LE NEST, J.F., GANDINI, A., CHERADAME, H., *Makromol. Chem., Rapid Commun*, Vol. 4, 497, (1983).
- (35) LEVEQUE, M., LE NEST, J.F., GANDINI, A., CHERADAME, H.J., *Power Sources.*, Vol. 14, 27, (1985).
- (36) SORENSEN, P.R., JACOBSEN, T., *Solid State Ionics*, Vol. 9+10, 1147, (1983).
- (37) SEQUEIRA, C.A.C., *Portugaliae Electrochimica Acta*, Vol. 3, 81, (1985).
- (38) SKOTHEIM, T., LUNDSTROM, I., *J. Electrochem. Soc.*, Vol. 129, 894, (1982).

- (39) ARMAND, M.B., DUCLOT, M.J., RIGAUD, Ph., *Solid State Ionics*, Vol. 3+4, 429, (1981).
- (40) SEQUEIRA, C.A.C., NORTH, J.M., HOOPER, A., *Solid State Ionics*, Vol. 13, 175, (1984).
- (41) RIGAUD, Ph., Thesis, University of Grenoble, (1980).
- (42) HOOPER, A., NORTH, J.M., *Solid State Ionics*, Vol. 9+10, 1161, (1983).
- (43) WEST, K., ZACHAU - CHRISTIANSEN, B., JACOBSEN, T., ATLUNG, S., *J. Electrochem. Soc.*, Vol. 132, 3061, (1985).
- (44) OWEN, J.R., MASKELL, W.C., STEELE, B.C.H., NIELSEN, T.S., SORENSEN, O.T., *Solid State Ionics*, Vol. 13, 329, (1984).
- (45) GAUTHIER, M., FAUTEUX, D., VASSORT, G., BELANGER, A., DUVAL, M., RICOUX, P., CHABAGNO, J.M., MULLER, D., RIGAUD, Ph., ARMAND, M.B., DEROO, D., *J. Power Sources.*, Vol. 14, 23, (1985).
- (46) BLONSKY, P.M., SHRIVER, D.F., *J. Am. Chem. Soc.*, Vol. 106, 6854, (1984).
- (47) ALLCOCK, H.R., AUSTIN, P., BLONSKY, P.M., SHRIVER, D.F., *Solid State Ionics*, Vol. 18+19, 258, (1986).
- (48) KILLIS, A., LE NEST, J.F., GANDINI, A., CHERADAME, H., *J. Polymer Sci.*, Vol. 19, 1073, (1981).
- (49) KILLIS, A., LE NEST, J.F., GANDINI, A., CHERADAME, H., COHEN-ADDAD, J.P., *Polymer Bulletin*, Vol. 6, 351, (1982).
- (50) WESTON, J.E., STEELE, B.C.H., *Solid State Ionics*, Vol. 7, 75, (1982).
- (51) MAC CALLUM, J.R., SMITH, M.J., VINCENT, C.A., *British Patent Application*, No 8418209, (1984).
- (52) VINCENT, C.A., GRAY, F.M., MAC CALLUM, J.R., *Solid State Ionics*, Vol. 18+19, 252, (1986).