

Cationic conductivity and relaxation processes in solid polymer electrolytes with lithium perfluoroalkyl sulfonate or sulfonato end-capped poly(ethylene oxide)

T. Hamaide* and C. Le Deore

Laboratoire des Matériaux Organiques, CNRS, BP 24, 69390 Vernaison, France
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Blends of lithium perfluorinated sulfonate, $C_8F_{17}SO_3Li$, or sulfonato end-capped poly(ethylene oxide), $PEO(SO_3Li)_2$, with high molecular weight PEO have been used as solid polymer electrolytes. In these materials, either the anion is bulky enough or is anchored to a polymer backbone to expect the anionic transport number to be equal to zero, so that only the cation contributes to the current transport. In addition, the fluorine atoms in the first anion would decrease the ion pairing whereas the second structure may be seen as a self-solvating anion, bringing the oxygen atoms required for the solvation of the lithium cation. $PEO(SO_3Li)_2$ has been synthesized by reaction of PEO alcoholate with propane sultone. These solid polymer electrolytes have been characterized by d.s.c., X-ray diffraction and complex impedance spectroscopy. The conductivities at room temperature are around $10^{-7} S cm^{-1}$, of the same order of magnitude as solid polymer electrolytes with only one mobile ion. Beside the resistances, some relevant parameters of the electrochemical behaviour (relaxation times, dispersive indexes) have been derived from analysis of complex impedance spectra and tentatively interpreted in the framework of charge carrier transport in heterogeneous electrolytic media in order to yield information about the morphological state of the materials.

(Keywords: solid polymer electrolytes; single ion conductor; grafted sulfonates; relaxation processes; impedance spectroscopy analysis)

INTRODUCTION

The interest devoted to solid solutions of alkali metal salts in linear polyethers for electrochemical devices has been growing for more than a decade; the papers presented at a recent symposium clearly showed that a lot of work remains to be done, particularly in the field of new polymers¹. Although one of the main questions is how to preserve, at room temperature, the metastable amorphous phase required for the transport of the ionic carriers during the ageing of the solid polymer electrolyte², problems connected with the mobility of both anion and cation in the solid electrolyte remain to be overcome. Indeed, different transport numbers lead to the building of space charges so that the chemical potentials of the ions are different not only at the electrode-electrolyte interfaces, but also inside the heterogenous polymer electrolyte. The current density is then greatly limited and consequently so too is their use for devices under d.c. polarization. Many studies have shown that anion mobility is generally higher than that of the cation, particularly when strong interactions occur between the cation and chelating moieties such as the ethylene oxide units³. For example, the dependence of the cationic transport number on various parameters, such as the counterion, the temperature and the salt concentration, has been studied or reviewed by several authors^{4,5}.

In order to overcome these drawbacks, Armand⁶ suggested the use of large anions, the mobility of which is reduced, or ions anchored either on a polymer backbone or on a pendant group on the polymer so that the transport number of their counterion would be unity. Several authors followed this idea and polymer backbones with anchored anions have been synthesized; for instance, poly(styrene sulfonate) was used by Hardy and Shriver⁷. Lithium salts of carboxylic acids linked to polymer backbones were reported by Watanabe *et al.*⁸. Polycationic supports with a mobile anion were also investigated^{9,10}.

Nevertheless, many polymer structures display a rather high glass transition temperature, T_g , so that the addition of low molecular weight polymers, such as polyethylene glycols, as plasticizers is required in order to reach an appreciable level of conductivity^{9,10}. Moreover, these polymers generally act as insulators since their backbone structures do not promote salt solvation. Incompatibility and hence demixing processes may also occur, owing to the great difference in the chemical structure between poly(ethylene oxide) (PEO) and ion-bearing polymers. Comb-shaped polymers with oligo-oxyethylene chains were used to lower the T_g and bring a supplementary contribution to the salt solvation. These polymers can also be seen as an attempt to separate the grafted anion from the polymer support by long PEO side chains, but it does not prevent the demixing processes of the main chains in all cases. Tsuchida and co-workers^{11,12}

* To whom correspondence should be addressed

used copolymers such as poly[lithium methacrylate-co-oligo(oxyethylene) methacrylate]. Zhou *et al.*¹³ described comb-shaped polysiloxanes with both oligo-oxyethylene chains and sodium sulfonate functions as pendant groups. Le Nest *et al.*¹⁴ included phosphate ions and propylene carbonate in polyether networks. In order to decrease the ion-pairing, Bannister *et al.*¹⁵ reported lithium salts of various perfluorinated carboxylic acids, as well as alkylsulfonic and perfluorocarboxylic groups grafted on polymethacrylate supports. Nevertheless, it must be borne in mind that these polymers must preserve good mechanical properties in order to be easily handled.

Continuing work previously reported¹⁶, this paper deals with the characterization and electrochemical properties of blends of lithium salts with a higher molecular weight PEO. Two lithium salts have been used, namely a large perfluorinated sulfonate lithium salt, $C_8F_{17}SO_3Li$, and a lithium sulfonate end-capped PEO, referred to as $PEO(SO_3Li)_2$, the cation transport number of which is close to unity. The first salt was interesting to test because the fluorine atoms must decrease the ion pairing while the second anion can be seen as a self-solvating anion, in the sense that it brings the oxygen atoms required for the lithium cation.

The relevant parameters of the electrochemical behaviour have been derived from analysis of complex impedance spectra and have been tentatively interpreted in the framework of charge carrier transport in heterogeneous electrolytic media in order to yield information about the morphological state of the materials.

EXPERIMENTAL

Synthesis and preparation of materials

$C_8F_{17}SO_3Li$ was supplied by Atochem Corp. The solvents were dried according to the usual procedures. PEO ($M_w=600$) was dried by azeotropic benzene distillation and then dissolved in tetrahydrofuran (THF). Propane sultone was distilled under vacuum just prior to use. The experiments were carried out under an argon atmosphere in previously argon-purged flasks.

The sulfonate end-capped PEO was synthesized by deactivation of the PEO alcoholates, previously obtained by reaction of PEO with the lithium dihydronaphthylide, with a slight excess of propane sultone in THF for 2 days at room temperature¹⁷. The resulting polymer was purified by three reprecipitations in heptane, dried under vacuum and characterized by elemental analysis, i.r. spectroscopy (ν_aSO_3 , 1213 cm^{-1}) and 1H n.m.r. (the protons of the $CH_2CH_2CH_2SO_3^-$ group appear at $\delta=2$, 2.9 and 3.3 ppm). The absence of propane sultone in the polymer was also checked by n.m.r.

Various amounts of the lithium salt, either $PEO(SO_3Li)_2$ or $C_8F_{17}SO_3Li$, and high molecular weight PEO ($M_w=900\,000$) were mixed in acetonitrile in a glove box under argon and the solid polymer electrolytes were obtained by casting the solution on a PTFE plate.

Measurements

X-Ray diffraction measurements were carried out on a Rigaku diffractometer. The samples were exposed to $CuK\alpha$ radiation at room temperature. The intensity of the diffraction lines was plotted against the diffraction angles, 2θ , from 10° to 30° .

Differential scanning calorimetry (d.s.c.) was performed with a Setaram analyser model DSC 101. The heating rate was 5°C min^{-1} . Samples were taken from

the electrolyte membranes and sealed in aluminium capsules in the glove box.

The experimental electrochemical cells were made by pressing the membranes ($\sim 200\ \mu\text{m}$ thickness) between two nickel electrodes and packing them in a button cell (20 mm diameter, 2 mm thick). Impedance measurements were carried out using a 1255 frequency response analyser (Schlumberger Solartron) connected to a 1286 electrochemical interface (Schlumberger Solartron) over the frequency range 0.1 Hz to 200 kHz. Experiments were monitored from a Tandy 1000 microcomputer. Data were stored on disks and retrieved for later treatment. The impedance spectra were analysed by least squares methods using either a circular regression or a non-linear least squares procedure¹⁸ depending on the shape of the impedance spectra.

RESULTS AND DISCUSSION

Polymer electrolytes based on $C_8F_{17}SO_3Li$

This anion was expected to be substantially blocked under an electrical perturbation, because of its bulkiness, while both the sulfonate function and the fluorine atoms would decrease the degree of ion pairing and enhance the concentration of lithium cations required for the transport of current.

X-ray diffraction patterns of $PEO-C_8F_{17}SO_3Li$ mixtures with various stoichiometries are depicted in Figure 1. The most important lines of the salt appear at

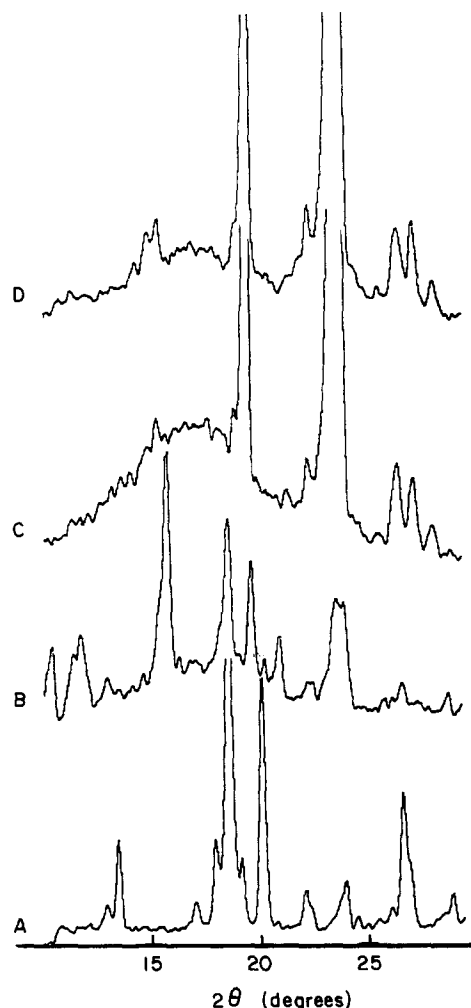


Figure 1 X-ray diffraction patterns of various stoichiometries of $PEO-C_8F_{17}SO_3Li$ mixtures. $[O]/[Li^+]$: A, 0; B, 5; C, 15; D, 50

$2\theta = 13.44^\circ, 18.61^\circ, 20.15^\circ$ and 26.76° . Adding the salt to PEO at low content ($[\text{O}]/[\text{Li}^+] > 5$) does not alter the characteristic diffraction pattern of the pure PEO, the main diffraction lines of which appear at $2\theta = 18.68^\circ$ and 23.66° . The PEO-salt complex with a $[\text{O}]/[\text{Li}^+]$ molar ratio = 5 displays new lines at $2\theta = 11.86^\circ, 15.84^\circ$ and 20.97° while the diffraction lines of both salt and PEO have almost disappeared. This new diffraction pattern, superimposed on the characteristic pattern of pure PEO and salt, suggests that a new crystalline complex is formed between the salt and PEO near the stoichiometry $[\text{O}]/[\text{Li}^+] = 5$.

These results are consistent with the d.s.c. results (Figure 2). The pure perfluorinated salt displays two main melting endotherms at 66 and 154°C (curve A; the little endotherm shown at 74°C disappears after the first thermal treatment, i.e. heating followed by cooling). The mixture with $[\text{O}]/[\text{Li}^+] = 5$ exhibits two broad endotherms at 59 and 102°C (curve B). The other mixtures ($[\text{O}]/[\text{Li}^+] > 5$) display only one sharp melting endotherm which rises from 62 to 68°C (curve C, $[\text{O}]/[\text{Li}^+] = 20$). In addition, the second endotherm of the salt which appeared at 154°C has quite disappeared, indicating that salt is miscible with PEO.

Typical complex impedance spectra at various temperatures are shown in Figure 3. They are characterized by a high frequency depressed semicircle followed by a low frequency straight line, the interpretation of which has been dealt with previously^{19,20}. The semicircle is attributed to relaxation processes occurring in the bulk electrolyte and can be described by the usual dispersion equation:

$$Z(\omega) \propto 1/(1 + (j\omega\tau)^{1-\alpha})$$

while the straight line is ascribed to the double layer capacitance due to the blocking character of the nickel electrodes and obeys the equation:

$$Z(\omega) \propto 1/(j\omega\tau)^{1-\beta}$$

The intersection of the straight line with the real axis gives the d.c. resistance. The conductivity is around $10^{-7} \text{ S cm}^{-1}$ at room temperature and its temperature dependence follows an Arrhenius-type behaviour with linear segments separated by a transition zone (Figure 4),

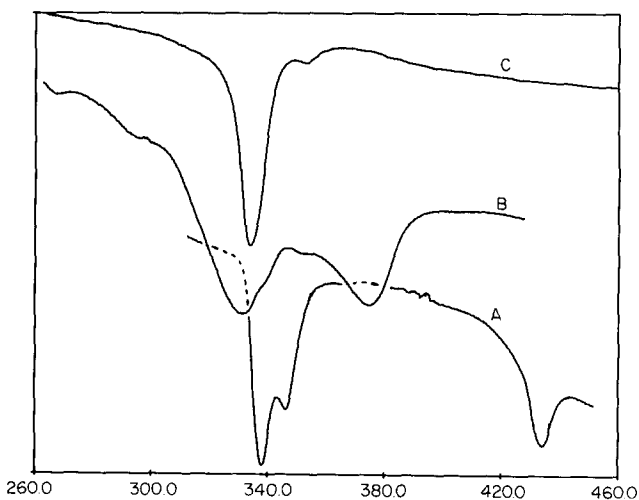


Figure 2 D.s.c. heating curves for the pure $\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}$ (A) and for two $\text{PEO}-\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}$ mixtures with $[\text{O}]/[\text{Li}^+] = 5$ (B) and 20 (C)

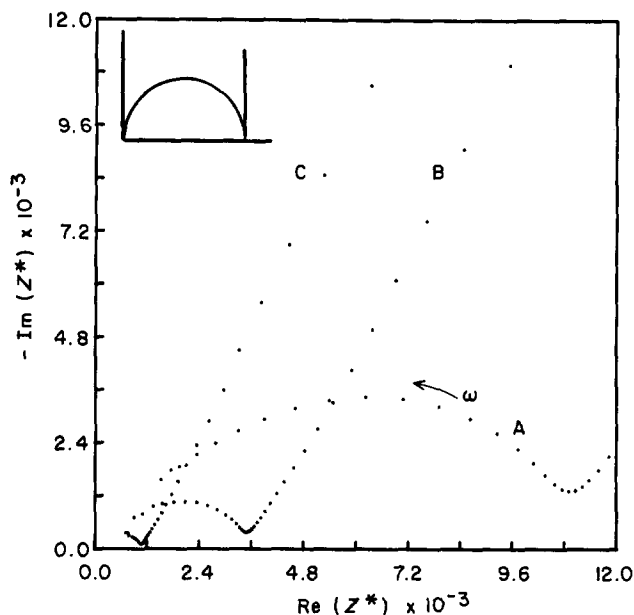


Figure 3 Typical impedance spectrum of a $\text{Ni}/\text{PEO}-\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}/\text{Ni}$ cell at various temperatures: A, 34°C ; B, 43°C ; C, 51°C . The insert shows a theoretical impedance spectrum (the equivalent circuit is a parallel RC circuit)

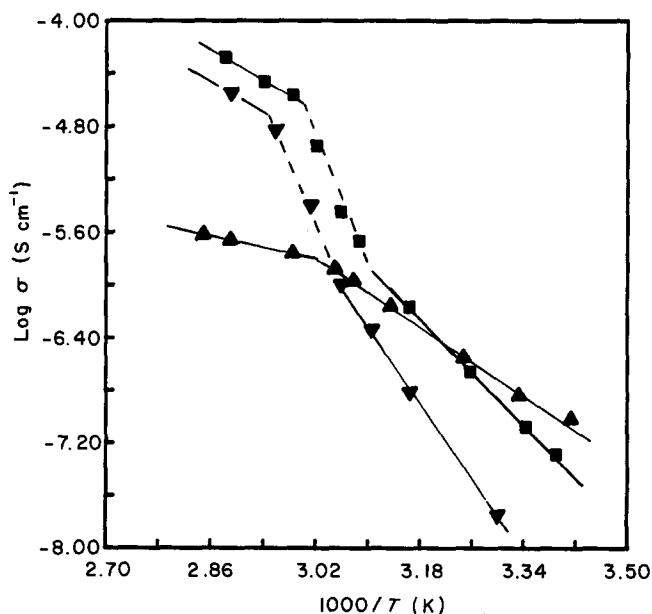


Figure 4 Temperature dependence of the conductivity of some $\text{PEO}-\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}$ solid polymer electrolytes. $[\text{O}]/[\text{Li}^+]$: \blacktriangle , 5; \blacktriangledown , 30; \blacksquare , 50

which corresponds to the temperature of the onset of the melting zone in the d.s.c. experiments. Such a feature was reported with the $\text{PEO}-\text{LiCF}_3\text{SO}_3$ system by Robitaille and Fauteux²¹ who ascribed this discontinuity to a eutectic melting temperature. The activation energies are 0.7–1.4 eV in the low temperature range and 0.2–0.6 eV above the melting temperature of the crystallized domains (Table 1). Except for $[\text{O}]/[\text{Li}^+] = 5$, these values are in the same range as those found by Zahurak *et al.*²² for the $\text{PEO}-\text{LiCF}_3\text{SO}_3$ complexes. The temperature dependence of the conductivity of the complex with $[\text{O}]/[\text{Li}^+] = 5$ does not follow the same trend as the other complexes; the conductivity becomes particularly low above the melting zone while it was better at low temperature, there is very little discontinuity between the

Table 1 Activation energies (eV) of the ionic conductivity for low and high temperature ranges.

| [O]/[Li ⁺] | C ₈ F ₁₇ SO ₃ Li | | | PEO(SO ₃ Li) ₂ | | | |
|------------------------|---|------|------|--------------------------------------|------|------|------|
| | 5 | 30 | 50 | 15 | 21 | 70 | 93 |
| Low temp. range | 0.68 | 1.43 | 1.00 | 0.91 | 1.29 | 0.59 | 0.62 |
| High temp. range | 0.19 | – | 0.54 | 0.31 | 0.16 | 0.30 | 0.17 |

two domains, and it displays the lowest activation energies.

The conductivity is lower than that obtained with the lithium trifluoromethylsulfonate usually used in polymer electrolytes and this may be connected with the fact that the anionic transport number is assumed to be close to zero. Nevertheless, the conductivity levels appear higher in this temperature range than those obtained by Bannister¹⁵ with the lithium perfluoroalkyl carboxylates CF₃(CF₂)_nCO₂Li (*n*=0, 1, 2), although the perfluoroalkyl chain is notably longer in our case (*n*=7). The decrease in the volume fraction of PEO due to the longer alkyl chain is advantageously balanced by the lower degree of ion-pairing due to the sulfonate group.

It should be noted that the increase in conductivity does not follow the increase in the lithium content in the low temperature range, which may be interpreted in terms of a diminution of available lithium cations for the current transport, probably due to the ionic associations.

Analysis of the high frequency depressed semicircle can be made using a circular regression procedure¹⁸. As depicted in Figure 3, heating the electrochemical cell causes a shift of relaxation times towards the high frequencies, because of the enhancement of the transfer processes, so that the semicircle can no longer be analysed above 50°C.

A relaxation process is characterized by a time constant, $\tau = 1/2\pi f_c$, which is generally defined as the inverse of the rate constant of an exchange process¹⁹. Due to the heterogeneous character of the bulk electrolyte and the unequal mobility of both ions, space charges are created and located everywhere inside the electrolyte. The accumulation and depletion rate of the space charges depends on the frequency of the applied electrical field and leads to relaxation processes. The location of these exchange processes can be seen as an interface where energy transfer takes place (see the Appendix). Therefore, these relaxation times may be related to the mobility of the charge carriers and the level of conductivity: the highest τ and the lowest σ . Typical values of the relaxation times are around 10⁻⁵ s (Figure 5), which is a value usually found with other materials²³. The temperature dependence may be described by an Arrhenius-type behaviour with an activation energy between 0.6 and 1.9 eV, which is of the same order of magnitude as noted for the temperature dependence of the conductivity.

Figure 6 and 7 display the deviations of the actual impedance spectra with respect to a theoretical profile (an undepressed semicircle). Figure 6 depicts how the phase angle ψ connected to the depressed semicircle depends on the salt content and the temperature (in a low temperature range below 50°C). This phase angle is classically ascribed to a distribution of relaxation times and related to the dispersive index α by $\psi = \alpha\pi/2$, but may also be interpreted in the framework of fractal geometry by assuming $1 - \alpha = 1/d$, where *d* is the fractal

dimension of the interface on which the energy transfer takes place^{24,25}

In this low temperature range, it is seen that the lower the value of ψ , the better the ionic conductivity. The transport of the charge carriers depends directly on the dimension of the interface on which the relaxation processes occur. On the other hand, ψ decreases as the temperature increases. Besides the enhancement of ionic mobility inside the amorphous domains of the electrolyte due to the thermal agitation, heating causes a diminution of the heterogeneous character of the bulk electrolyte which also contributes to the improvement of the conductivity level. The term heterogeneous must be related to the distribution of crystalline domains as well as that of the space charges throughout the bulk

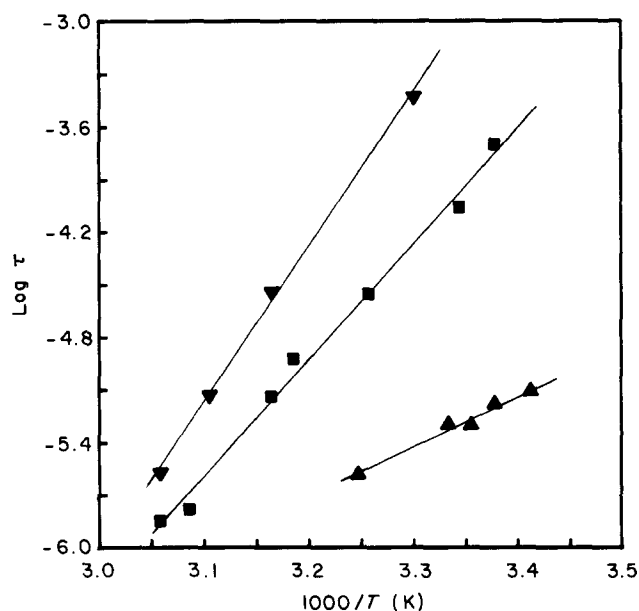


Figure 5 Temperature dependence of the time constant $\tau = 1/2\pi f_c$ related to the high frequency semicircle for PEO-C₈F₁₇SO₃Li electrolytes. Symbols as for Figure 4

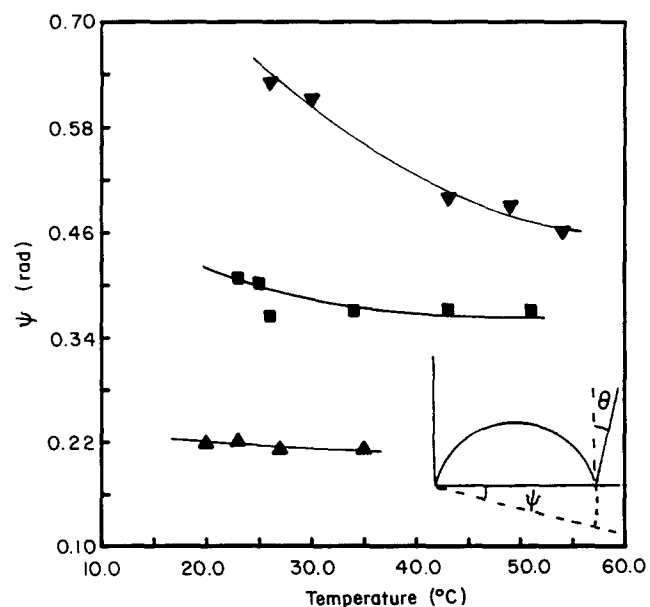


Figure 6 Phase angle ψ of the depressed semicircle observed for impedance spectra of the Ni/PEO-C₈F₁₇SO₃Li/Ni cells. Symbols as for Figure 4

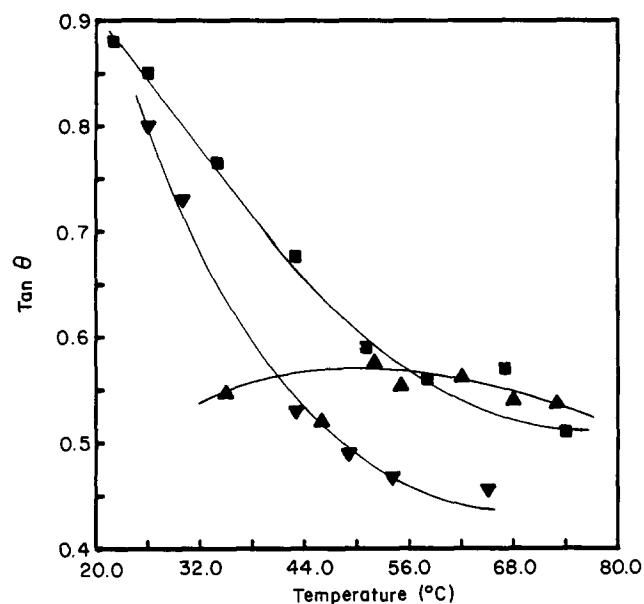


Figure 7 Deviation of the capacitive straight line with respect to the theoretical one for the impedance spectra of the Ni/PEO-C₈F₁₇SO₃Li/Ni cells. Symbols as for Figure 4

electrolyte. The same trend is observed with the slope ($\tan \theta$) of the capacitive straight line (Figure 7); it may be interpreted in terms of modifications of the electrolyte part of the electrolyte/electrode interface²³, since there is no change on the metal electrode in this temperature range, although the metal electrode may induce another behaviour in the crystallization processes. It is worth noting the insensitivity to temperature of the interface dimensions when $[O]/[Li^+] = 5$ in bulk as well as in electrodes; this might explain the particular behaviour of this electrolyte.

Synthesis and characterization of the sulfonato end-capped PEO

Sulfonato end-capped PEO, PEO(SO₃Li)₂, was synthesized in an attempt to overcome the incompatibility problems induced when using other kinds of polymer backbones. Indeed, one relevant feature of these telechelic PEO is that they themselves bring the ether groups that are required to solvate the lithium salt so that the monomer to salt ratio can be kept at a constant value without the dilution effect (that is without decreasing the PEO volume fraction) when another non-solvating polymer backbone is added. Moreover, the lithium cation can be solvated simultaneously by PEO and PEO(SO₃Li)₂, which may also improve the homogeneity.

Some reactions have been reported in order to graft the sulfonate function, namely the action of sodium sulfite, Na₂SO₃, on bromoalkyls²⁶ or sodium bisulfite, Na₂S₂O₅, on glycidyl groups²⁷. Sodium sulfonates are obtained in this way and cation exchange is required if the lithium salt is desired. In addition, these reactions have to be carried out in the aqueous phase and require additional azeotropic drying with benzene. It should also be noted that the opening of the epoxy ring leads to an alcohol group which may become another passivation factor when putting this material on a lithium electrode. Polymer electrolytes were nevertheless synthesized according to this latter procedure and impedance measurements were performed with copper electrodes¹³.

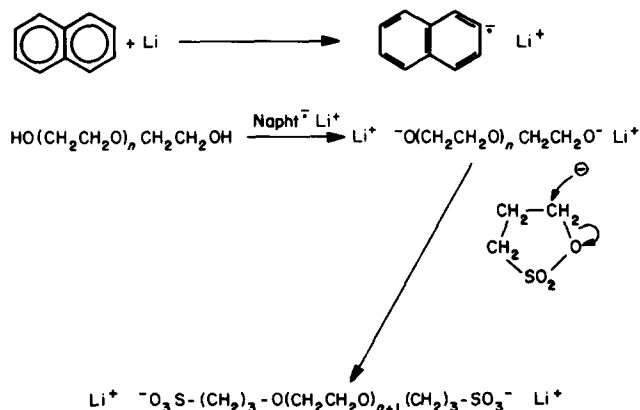
On the other hand, sultones react readily with alcohols to form the sulfopropyl derivative with a good yield¹⁷, according to the ring-opening reaction described in Scheme 1, although the transposition to macromolecules depends on the system being considered. For example, poly(vinyl alcohol) gives poor yields, because of the neighbouring-group effects^{28,29}, while reaction with PEO can be carried out easily with good yields¹⁷. The sulfonate anion is a poor nucleophilic agent, so that the grafted anion is unable to open another sultone ring. Moreover, using the naphthylide radical anion as the base allows the desired alkali counterion to be chosen without any cation exchange¹⁶.

Owing to its marked ionic character, the polymer is recovered as a powder after evaporation of the solvent although the starting PEO is a viscous liquid. This feature is also observed with lower semi-telechelic sulfonato end-capped PEO, such as CH₃(OCH₂CH₂)₃(CH₂)₃SO₃Li, or betaine end-capped polyisoprenes, and is clearly attributed to ionic aggregates able to cause physical crosslinks in the case of telechelic polymers³⁰. At low ionic concentration, these polymers can be considered as ionomers, the bulk and solution properties of which are well known^{31,32}.

Crystallinity can be detected by wide-angle X-ray diffraction, confirmed by d.s.c. which shows a single sharp endotherm at 52°C related to the melting of the crystalline phase. The low-angle diffraction displays Bragg spacing lines which are typical of a lamellar structure. The measured intersheet spacing was 45 Å, which is in a good agreement with the (7/2) helix configuration with a length of 19.3 Å for seven monomer units^{33,34}, if taking account of the lithium propylsulfonate groups at both ends of the chain. Ionic interactions cause the PEO chain to be fully extended, which allows crystallization to take place more easily.

X-ray diffraction patterns of the various stoichiometries of PEO-PEO(SO₃Li)₂ display the same lines as those of high molecular weight PEO without any noticeable change in the intensities. Thus the addition of the sulfonato end-capped PEO does not alter the structure of the crystallized PEO. This result was noticed previously when mixing styrenic macromonomers of PEO CH₂=CH-C₆H₄-CH₂-O-(CH₂CH₂O)_nCH₃ with high molecular weight PEO³⁵.

At low salt content, the d.s.c. thermograms exhibit a melting endotherm, the temperature of which depends on the mixture composition, with a minimum at 61°C



Scheme 1 Functionalization of PEO by propane sultone

for the stoichiometry $[O]/[Li^+] = 21$. At higher salt concentration ($[O]/[Li^+] = 10$), an additional small endotherm appears at 51°C, which can be related to the pure $PEO(SO_3Li)_2$ component.

The existence of clusters in these systems remains to be physically proved, but some points can be advanced in favour of them. In particular, results related to investigations on sulfonated ionomers can be used to attempt to explain the behaviour of our compounds.

Ionomers such as lightly sulfonated polystyrene (PS) exhibit properties, either in solution or in bulk, due to the interaction of ionic groups randomly spaced along the backbone^{36,37}. Provided the solvent is not too polar, intermolecular associations are observed. These associations can also take place in the bulk and lead to the microphase separation of ionic microdomains scattered in a PS matrix. Because our ionic polymers are obtained by reaction of propane sultone on both ends of a PEO chain and mixed inside a PEO solid solution, our mixtures could be considered as a more or less sulfonated PEO instead of sulfonated PS. If the extent of clustering depends first on the dielectric constant of the polymer matrix, PEO would slightly enhance the solubility of the ionic polymer since its dielectric constant is higher than that of PS: $\epsilon = 5$ for PEO compared to 2.6 for PS. Nevertheless, ϵ remains too low to assure a good solvation of the ionic domains. As an example, microphase separations have been observed with random ethyl acrylate-sulfonatopropylbetaine copolymers in which the poly(ethyl acrylate) matrix has a higher polarity ($\epsilon = 7$)³⁸. Another argument in favour of intermolecular associations is the observation that the solutions of $PEO(SO_3Li)_2$ in acetonitrile ($\epsilon = 37.5$) are turbid, indicating poor solvation of the polymer and thus intermolecular associations, despite the high polarity of this solvent. Addition of PEO does not make the acetonitrile solution clearer; this shows that interaction between PEO chains and the ionic groups of the telechelic PEO does not obviously enhance the solubility of the latter compounds. In fact, the formation of complexes between the PEO chains and the lithium salts is controlled by the entropy term (spatial organization of the PEO chain)³⁹, which would also contribute to the decrease of the lithium cations blocked inside the clusters by displacement of the equilibrium $(Li^+)_{agg} \rightleftharpoons (Li^+)_{free}$, and thus enhance the conductivity.

Interesting studies have been performed on mixtures of sulfonated PS and poly(vinylpyridine-co-styrene) or α,ω -diamino telechelic polyisoprenes, which clearly demonstrated a complexation between the aminated functional groups and the cations^{40,41} leading to interpolymer complexes. It was emphasized that these interactions are quite dynamic.

Impedance measurements on $PEO(SO_3Li)_2$ -based polymer electrolytes

Contrary to the previous case, the impedance spectra of solid polymer electrolytes with sulfonato end-capped PEO are characterized by two overlapped semicircles in the high frequency range followed by a low frequency straight line (Figure 8). In some cases, the impedance spectra can be seen as a more or less distorted semicircle, but when the electrochemical cell is heated, the two semicircles do not change in the same way; this implies that they are connected to two different transfer processes with different activation energies. It also means that the

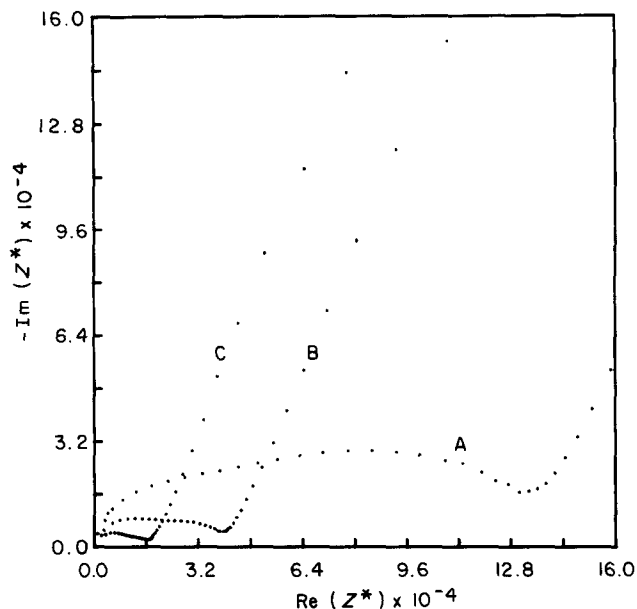


Figure 8 Typical impedance spectrum of a Ni/PEO- $PEO(SO_3Li)_2$ /Ni cell ($[O]/[Li^+] = 21$) at various temperatures: A, 36°C; B, 43°C; C, 50°C

two semicircles cannot be considered as a single distorted semicircle.

The high degree of overlap of these semicircles does not allow a simple analysis of the impedance data and the main relevant parameters of both semicircles were retrieved by using a non-linear least squares (NLLS) procedure. This was based on the optimization of a starting set of parameters in order to obtain better agreement with the experimental data¹⁸. Although simple in principle, some features deserve to be emphasized. The procedure may converge towards a set of parameters which have neither physical sense nor a good agreement with the impedance spectrum. On the other hand, it is based on a mathematical model which may be too simple to take into account all the characteristics of these heterogeneous systems.

Thus, the first step in checking the validity of the NLLS procedure is to simulate the impedance spectrum connected to the set of parameters given by the procedure and compare it with the experimental spectrum. As an example, a theoretical impedance spectrum has been calculated with the parameters extracted from the experimental one and the superimposition of both spectra is displayed in Figure 9. The very good agreement between experimental and calculated spectra highlights the validity of the NLLS procedure.

In addition, each of the parameters of the considered impedance spectrum must depend on a selected variable, for example the temperature or the salt content according to a reasonable behaviour law. Figures 10a and b depict the temperature dependences of both transfer resistances, Rt_1 and Rt_2 , derived from the NLLS procedure; the resistances are reasonably scattered around a straight line when plotted in the Arrhenius diagram and decrease with increasing temperature. Such a result strengthens the validity of the procedure.

The conductivities of these polymers are around $10^{-7} S cm^{-1}$ at room temperature, similar to those of siloxane comb polymers with sodium sulfonate groups anchored to pendant oligo-oxyethylene chains¹³. As previously observed with the same kind of electrolytes¹⁶,

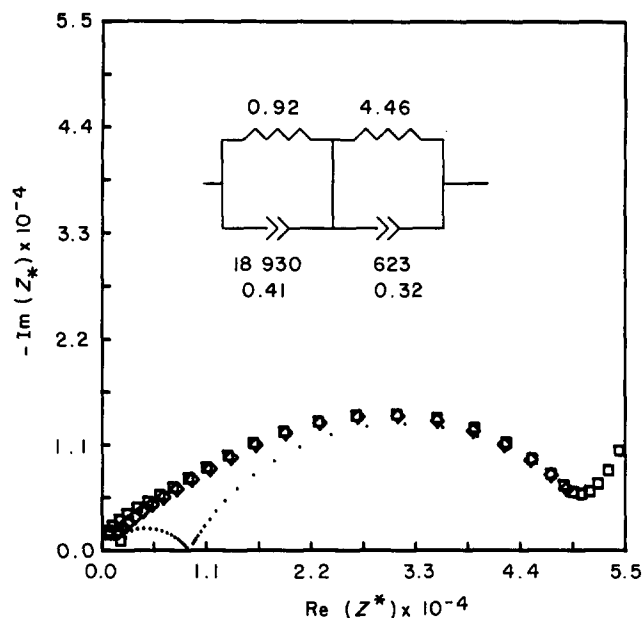


Figure 9 Typical impedance spectrum (\square) of a Ni/PEO-PEO(SO₃Li)₂/Ni cell ([O]/[Li⁺]=70; 33°C) and the simulation (\diamond) of the high frequency part (both overlapped semicircles) after a NLLS procedure. The insert depicts an equivalent circuit in which the constant phase elements (CPEs) are represented by a double arrow²⁴. Numbers below the CPE refer to the frequency f_c and the dispersive index α respectively. The CPE is defined in the Appendix. The dotted lines represent the impedance spectra which are related to both parts of the equivalent circuit, the sum of which gives the simulated spectrum

the conductivity shows an Arrhenius-type behaviour with two domains of temperature, below and above the melting point of the crystalline domains, and separated by a discontinuity (Figure 11). At low temperature, a good agreement is generally found between the intersection of the low frequency straight line and the second semicircle with the real axis. The activation energies are between 0.6 and 1.3 eV in the low temperature domain and between 0.16 and 0.31 eV above 60°C (Table 1). These values are in the same range as those found for the Solid Polymer Electrolytes with CF₃SO₃Li (ref. 22) and C₈F₁₇SO₃Li.

This Arrhenius-type behaviour has been observed by Bannister¹⁵ with poly(lithium perfluoroalkyl methacrylate) and dilithium hexafluoroglutarate. Conversely, sodium sulfonate groups anchored either on the oligo-xyethylene chains of a polysiloxane comb polymer¹³ or the PS with polyethylene glycol as plasticizer⁷, as well as the poly[lithium methacrylate-co-oligo(oxyethylene) methacrylate]¹¹ are usually described with a free-volume law (Vogel-Tammann-Fulcher (VTF) or Williams-Landel-Ferry (WLF) laws). These various temperature dependences can generally be correlated with the morphology of the solid electrolyte, an all-amorphous electrolyte showing a VTF behaviour, while conductivity in heterogeneous media is often described by an Arrhenius-type law.

In the low temperature range, the conductivity generally decreases when increasing the lithium content, due to a diminution of available lithium cations for the current transport because of ionic association. These associations can also be evidenced by the relaxation times. Figures 12a and b display the relaxation times connected with both semicircles, which appear at low temperature in the high frequency range. The first time constant value is between 2.5×10^{-5} and 3×10^{-6} s (Figure 12a) and can

be compared with previous experiments carried out with a PEO-lithium trifluorosulfonate ([O]/[Li⁺]=11) solid electrolyte pressed between two nickel electrodes²³. These experiments have shown that only one semicircle appeared at high frequencies, the time constant of which was around 1×10^{-5} s, and was associated with the relaxation processes occurring in the bulk heterogeneous electrolyte. In addition, the value of the capacitance that is associated with the relaxation time by $\tau = R_i C$ is about 0.1 nF, which is consistent with the previous results.

The second process exhibits relaxation times (Figure 12b) which are higher than the first one, between 5×10^{-5} and 6×10^{-4} s, with values of the related capacitances around 5 nF. These relaxation processes might tentatively be attributed to the cations blocked in the clusters. Dealing with Nafion perfluorosulfonate membranes and the formation of clusters, Datye *et al.*⁴² suggested a dipole layer, so that an electrostatic potential could be formed at the surface of the cluster. This potential may

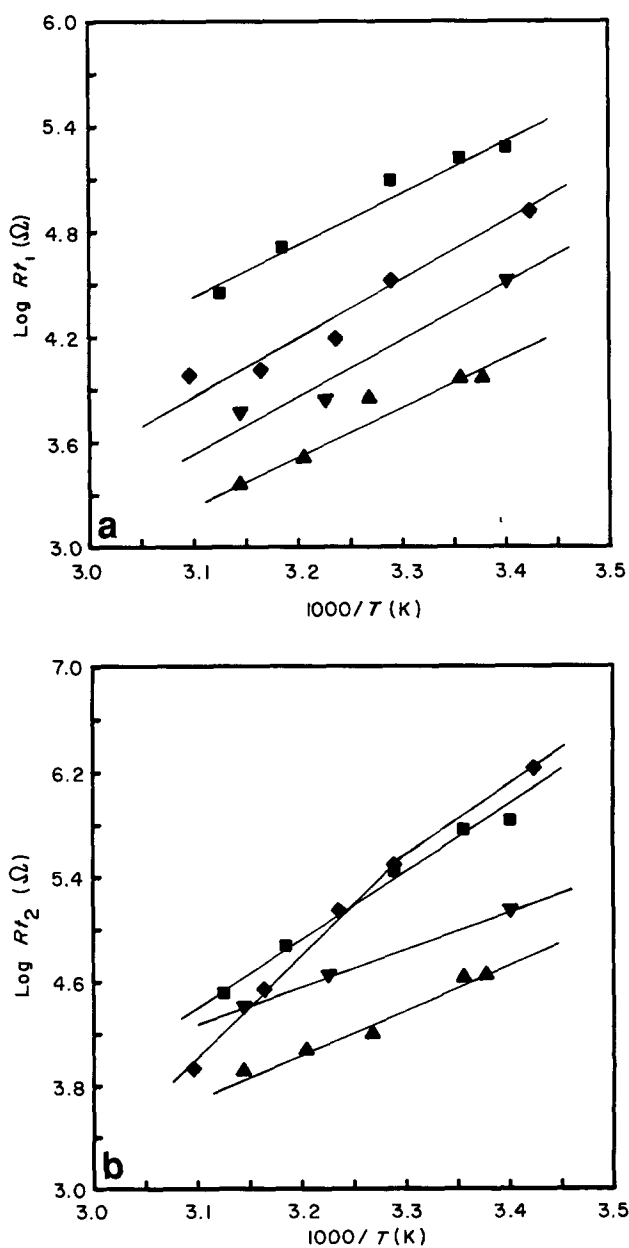


Figure 10 Temperature dependence of transfer resistances Rt_1 (a) and Rt_2 (b) after the NLLS procedure. [O]/[Li⁺]: \blacksquare , 15; \blacklozenge , 21; \blacktriangle , 70; \blacktriangledown , 93

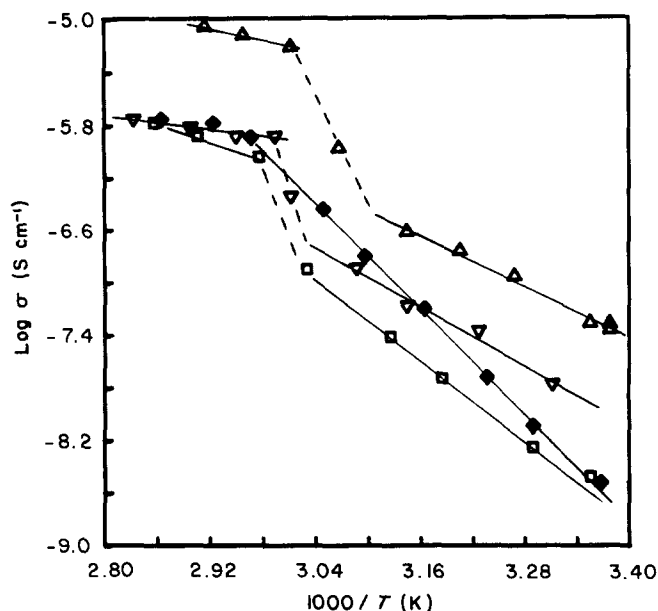


Figure 11 Temperature dependence of the conductivity of some PEO-PEO(SO₃Li)₂ solid polymer electrolytes. [O]/[Li⁺]: □, 15; ◆, 21; △, 70; ▽, 93

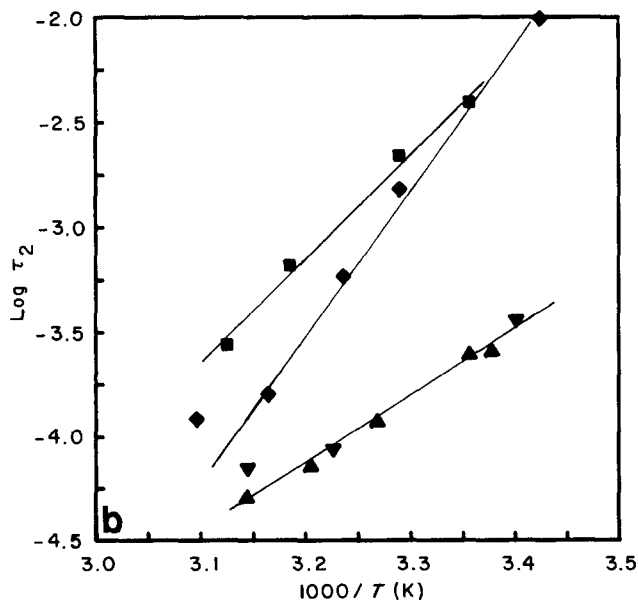
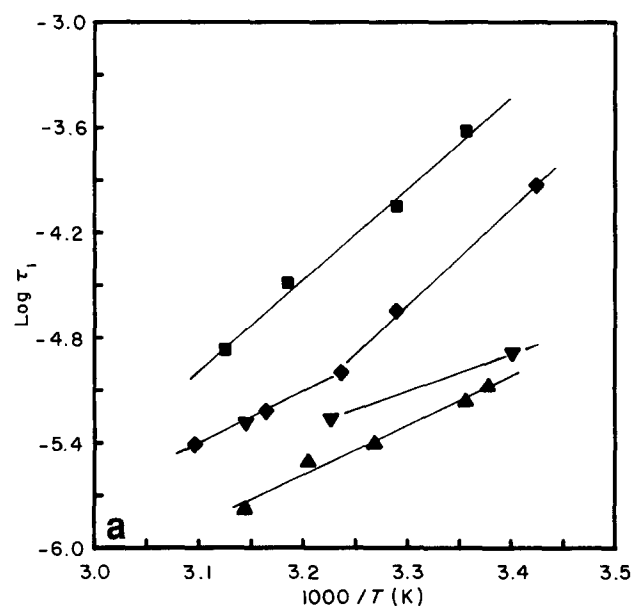


Figure 12 Temperature dependence of time constants τ_1 (a) and τ_2 (b). Symbols as for Figure 10

contribute to the ionic transport, the ions travelling by hopping between clusters. These clusters could therefore be seen as lithium reservoirs scattered inside the bulk electrolyte. In that case, the geometrical parameters of the surface of the clusters which are involved in these exchange processes would obviously be quite different from those of a simple electrolyte/metal electrode interface and hence the related capacities. A critical analysis of Datye *et al.*'s cluster model was given by Mauritz⁴³, suggesting that this model might be limited to non-perfluorinated systems in the dry state, which is the case for these solid polymer electrolytes.

CONCLUSIONS

Although the perfluorinated lithium sulfonate, C₈F₁₇SO₃Li, is expected to display a lower degree of ion pairing due to the fluorine atoms, the sulfonate end-capped PEO membranes are probably more interesting in consideration of solid polymer electrolytes because of their ability to solvate the cations by themselves. The conductivities at room temperature are around 10⁻⁷ S cm⁻¹, of the same order of magnitude as other solid polymer electrolytes with only one mobile ion, but the ring opening reaction of the sultone by the alcoholate can easily be transposed to any polyethylene glycol or polyethylene glycol monoalkyl ether, which makes this synthesis quite versatile in fixing the ratio [O]/[Li⁺] at any desired value without undergoing a dilution effect. The applications of these new electrolytic systems in electrochemical devices with d.c. polarization are now under investigation.

The main drawback seems to be the association of the ionic moieties to form clusters, which decreases the concentration of available 'free' lithium cations for ion transport. On the other hand, one can take advantage of the fact that these clusters can control some mechanical properties by means of physical crosslinks. As suggested by some authors^{7,13}, small polyethylene glycols could be used to dissociate the clusters by hydrogen bonds and increase the number of free lithium cations, but mechanical properties might be lost. Therefore a balance between the concentration of clusters and that of polyethylene glycol has to be found. A mixture of telechelic and semitelechelic sulfonate end-capped PEO can also be considered. Dipolar aprotic functions with high dielectric constants would also be used instead of polar protic moieties, but it must be emphasized that our first attempts in this direction, with solid polymer electrolytes based on the system LiCF₃SO₃/PEO/PEO macromonomer, were unsuccessful, since no improvement in conductivity levels was observed. Nevertheless, their influence on systems displaying only one mobile ion has to be fully investigated.

Impedance spectroscopy can be seen as an additional method allowing investigation of the evolution of morphological processes in ion-containing polymers, such as ionomers and polyelectrolytes. Impedance methods have already been used for dielectric relaxation studies of ion motions in ionomers by Mauritz^{44,45} who derived the complex dielectric constants from measured values of resistance and capacitance. The above study shows that it is also possible to investigate bulk electrolytes without further derivations.

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APPENDIX

Many papers have dealt with the interpretation of the impedance spectra of solid polymer electrolytes^{19,20}. In the simplest form, when the electrolyte is supposed to be quite homogeneous, the profile of the impedance spectrum depends on the electrolyte-electrode interface behaviour. In addition to these electrode processes, the heterogeneity of the bulk electrolyte can provide additional relaxation processes. A simplified model may be given by looking at an electrolytic domain where some crystalline zones are scattered in an amorphous domain. In that case, the conductivity may be explained in terms of a percolation process where the percolation threshold would depend on the extent of crystallinity. Under the applied electric field, the ions are forced to go through the pathway of least resistance, which will obviously be quite tortuous.

In this heterogeneous medium, both ions generally display a different transport number leading to space charges scattered in the bulk electrolyte. This space charge concept, first introduced by MacDonald⁴⁶ in his theoretical analysis of electrolytes with two ions displaying unequal mobilities, can easily be extended to a heterogeneous medium in which the space charges can also originate from the boundary amorphous regions between two crystalline domains where the motion of the ions are more or less blocked⁴⁷. The equivalent circuit of each boundary region may be depicted by a parallel RC circuit, similar to a non-blocking interface, and the overall impedance will be given by considering the individual impedances connected in series.

The various morphological states of the spherulites will induce a wide relaxation time distribution. The impedance spectra are generally depressed semicircles described by the usual dispersion equation:

$$Z^* = R/(1 + (j\omega\tau)^{1-\alpha})$$

where α is the dispersive index generally ascribed to the distribution of the relaxation times. The phase angle ψ , which measures the deviation of the impedance spectrum with respect to the simple theoretical profile, does not depend on the frequency (constant phase angle). The capacitance used in the equivalent circuit is replaced by a constant phase element, the main property of which is to provide a frequency-independent phase angle (see Figure 9).

Besides the macroscopic interpretations of the distribution of the relaxation times, another accurate theory was proposed by Le Méhauté and Crépy^{24,25}, who described the transfer of energy in the framework of the fractal geometry. In this theory, energy transfer takes place across an interface, the dimension of which is fractal, and which may be seen as the support of a discontinuity of the electrochemical potential due to the presence of space charges either at the electrolyte-electrode interface or in the bulk electrolyte. Assuming a self-similar medium, the dispersive index α is related to the phase angle of the semicircle by $\psi = \alpha\pi/2$ and a fractal dimension d may be derived by $1 - \alpha = (d)^{-1}$.