Performance limitations of polymer electrolytes based on ethylene oxide polymers

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Abstract

Studies of polymer electrolyte solutions for lithium-polymer batteries are described. Two different salts, lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) and lithium trifluoromethanesulfonate (LiTf), were dissolved in a variety of polymers. The structures were all based upon the ethylene oxide unit for lithium ion solvation, and both linear and comb-branch polymer architectures have been examined. Conductivity, salt diffusion coefficient and transference number measurements demonstrate the superior transport properties of the LiTFSI salt over LiTf. Data obtained on all of these polymers combined with LiTFSI salts suggest that there is a limit to the conductivity achievable at room temperature, at least for hosts containing ethylene oxide units. The apparent conductivity limit is 5×10^{-5} S/cm at 25°C. Providing that the polymer chain segment containing the ethylene oxide units is at least 5–6 units long, there appears to be little influence of the polymer framework to which the solvating groups are attached. To provide adequate separator function, the mechanical properties may be disconnected from the transport properties by selection of an appropriate architecture combined with an adequately long ethylene oxide chain. For both bulk and interfacial transport of the lithium ions, conductivity data alone is insufficient to understand the processes that occur. Lithium ion transference numbers and salt diffusion coefficients also play a major role in the observed behavior and the transport properties of these polymer electrolyte solutions appear to be quite inadequate for ambient temperature performance. At present, this restricts the use of such systems to high temperature applications. Several suggestions are given to overcome these obstacles. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Performance limitations; Polymer electrolytes; Ethylene oxide polymers

1. Introduction

Rigorous performance demands are made by battery engineers on organic electrolyte solutions in rechargeable lithium batteries. These materials, whether liquids or polymers, are in intimate contact with strongly reducing lithium metal or lithiated carbon and with reactive, highly oxidizing metal oxides related to materials widely used for catalysis in other fields of technology [1]. Transport of lithium ions through the bulk of the polymer and across the electrode interfaces must occur rapidly to achieve desired power density and without significant damage to either electrolyte solution or electrode, in order to obtain long cycle life. Both are necessary for applications such as the electric vehicle battery. Reactivity, inadequate lithium transport properties, and formation of dendrites at the lithium polymer interface during the charge cycle create serious challenges for the development of a successful system. Polymer electrolytes must also serve dual-duty as separators in cells, requiring excellent dimensional stability, in addition to these rigorous electrochemical properties. Nevertheless, the existence and excellent performance of remarkable materials such as Nafion™ provides hope that a solution to these difficult problems may exist.

Lithium metal batteries are the only systems considered capable of the long-range performance requirements for electric vehicle use. Polymer electrolytes based on poly-ethylene oxide (PEO), polypropylene oxide (PPO) and related polymers provide inherent safety advantages over liquid systems with lithium metal. However, these materials have limitations. They react with lithium metal and are

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oxidized at relatively modest potentials, thereby restricting the choice of positive electrode materials. The conductivities of the 'dry' polymer electrolytes remain stubbornly at values less than 10^{-4} S/cm at room temperature and salt diffusion coefficients, and lithium ion transference numbers also remain low. Furthermore, conductivities of polymer electrolytes are generally inversely correlated with glass transition temperatures (T_g) of the polymer, which implies poorer mechanical properties as the ionic conductivity improves. The poor transport properties of the ethylene oxide-based polymer electrolytes limit the application to high temperature uses such as EV batteries (80°C) and impede the development of the technology, as no ambient temperature uses can be introduced that can provide reliability data prior to scale-up to EV size.

It is the purpose of this paper to compare data on a number of different polymer electrolyte systems in an effort to elucidate the structural factors that limit performance. The structures are shown in Fig. 1. They are based upon ethylene oxide (EO) polymers that have a variety of architectures to which the EO units are attached. Most of these polymers are comb-branch in structure and have been reported previously in the literature. The results reported here are with lithium trifluoromethanesulfonate (LiTf) (LiCF$_3$SO$_3$) and the low lattice energy salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (LiN(CF$_3$SO$_2$)$_2$). Since polymer electrolytes prepared from the LiTFSI salt are the most known conductive at this time, these results are representative of the present limits of performance of polymer electrolytes for lithium batteries.
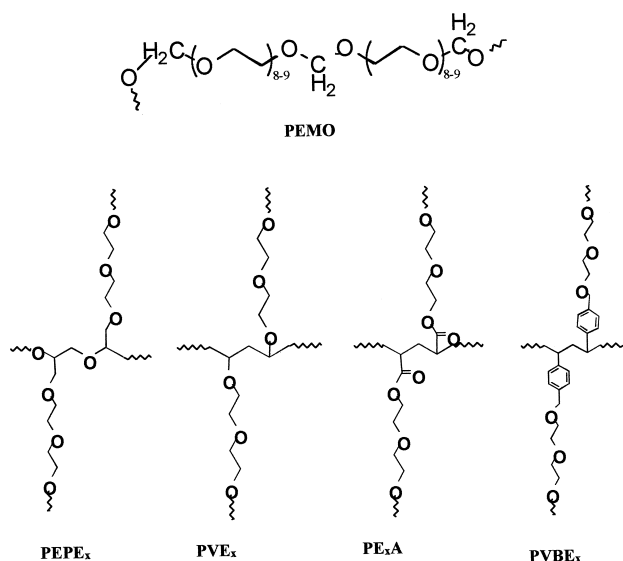

Fig. 1. Polymer structures, acronyms and nomenclature. PEMO = oxymethylene-linked PEG400; PEPE$_x$ = polyepoxide ether; PVE$_x$ = polyvinyl ether; PE$_x$A = polyacrylate ether; PVBE$_x$ = polyvinylbenzyl ether; x denotes the number of EO groups in the side chain.

2. Experimental

Cell cycling, polarization and diffusion measurements were carried out using an Arbin (College Station, TX, USA) BT 4020 multichannel cycler or a MacPile II (Biologic, Claix, France) multichannel potentiostat/galvanostat. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-7. All samples were prepared in the glove box and transferred to the DSC without exposure to air. Chemical analyses of monomers, polymers and salts were carried out using an HP5890 gas chromatograph (GC), gel permeation chromatography (GPC) (DMF solvent, Rainin HPXL, Knauer Differential Refractometer and a PLgel 10 cm Minimix-B column (PL Labs)) and a HP^{3D} capillary electrophoresis (CE) instrument, respectively.

For conductivity measurements, a Solartron™ SI 1254 four-channel frequency response analyzer and a 1286 electrochemical interface were used to measure the impedance of electrolyte films of known thickness in constant-volume cells with blocking electrodes. A Swagelok cell-holder design was used, which sealed the sample from the atmosphere. For films that were melt-processable, a spacer of known thickness was utilized, and the film was allowed to flow under heat and pressure until the spacer was completely filled. Cells were equilibrated in a convection oven with the temperature controlled to within ± 0.5°C, for at least 1 h prior to measurement. Measurements were taken at 10°C intervals between 30°C and 110°C; low temperature measurements (− 30°C, − 5°C) were carried out by placement of the cell in a laboratory refrigerator. Equilibration at − 30°C for at least 10 h was found to give the most reproducible results. The same cell-holders were used with lithium metal electrodes for DC experiments. All cell construction activities were carried out in a helium atmosphere with O$_2$ and H$_2$O concentrations < 1 ppm, which was scrupulously free of organic solvent vapors.

LiTFSI was a gift from 3M. LiTf was obtained from Aldrich Chemical. Both salts and polymers were dried under vacuum over P$_2$O$_5$ in a drying pistol and transferred to the glove box without exposure to atmosphere. For most polymers and salts, a drying temperature of 60°C was sufficient, but for LiTFSI, a temperature of 160°C was used to remove a component, perhaps a CO$_2$ complex, that could be observed in DSC measurements. Polymer films were prepared in a glove box designated for use with organic solvents. Solvents for preparation of polymer and salt solutions (dimethoxyethane or acetonitrile) were obtained from Burdick & Jackson, distilled in glass grade. Prior to use, they were dried in the glove box by percolation through a column of Super-activated Alumina (ICN). Polymer–salt solutions were cast on Teflon-coated glass with the aid of glass ring forms to contain the viscous liquid. The solvent was evaporated in the glove box and the resulting films fully dried under vacuum. The films

were then transferred in sealed containers to a solvent-free glove box for cell assembly.

Postmortem analysis of cycled cells was carried out by disassembly of the cell either in the glove box or outside. Polymer films were separated from the electrodes and both were dissolved in distilled water. The pH was adjusted with HCl to about 8–9 and the aqueous layer was continuously extracted with methylene chloride for analysis by GC(/MS), GPC and/or CE. The aqueous layer was analyzed by CE to detect and identify ionic species resulting from salt degradation. Samples were introduced to the GC by means of a cold, on-column inlet system to avoid any reactions in the injection process. Appropriate controls were carried out to ensure that observed products did not result from these procedures.

2.1. Preparation of oxymethylene-linked PEG 400 (PEMO)

Colorless, sticky and flow-resistant PEMO was produced using a Williamson ether synthesis technique [2]. Purification was accomplished by: (1) vacuum filtration of the reaction products from a methylene chloride solution, (2) wash of the methylene chloride with water ($3 \times$) in a separator funnel, (3) multiple fractionations from methylene chloride by slow addition of heptane, (4) drying at 80°C in vacuo over P_2O_5. The average molecular weights (Mw, Mn) were determined using GPC. Mw values were in the range of 100–150k with Mn $\sim$ 50k. The polymers were very viscous liquids at room temperature.

2.2. Preparation of polyvinyl ethers (PVE_x)

These were prepared using BF_3-etherate initiator [3–5] or an $Et_{1.5}AlCl_{1.5}$ initiator [6] with vinyl ether monomers. The latter system was employed to investigate living polymer conditions in an attempt to obtain high molecular weights. Monomers were prepared according to the literature [3,4,7]. Polymers were obtained with Mw = 30–100k and up to 300k when divinylether chain extenders were used. Only at the early stages of the reaction was a low polydispersity observed that indicated the presence of a living polymer. The polymers were very viscous liquids at room temperature.

2.3. Preparation of polyepoxide ethers ($PEPE_x$)

These materials were prepared according to the method of Andrei et al. [8] and Marchees et al. [9], using monomethylethyleneglycol epoxide monomers and potassium *tert*-butoxide as initiator. Polymers with Mw values in the range of 50–100k were obtained (up to 10^6 when diepoxide ether chain extenders were used). The polymers were very viscous liquids at room temperature.

2.4. Preparation of polyacrylate ethers ($PE_x A$)

Monomers were prepared by reaction of monomethyl (oligo-)ethylene glycols with acrolyl chloride. Chain lengths were defined from 2–6 EO units long by choice of the appropriate acrylate ether monomer. Polymerization was carried out in refluxing solution (methanol) using AIBN as initiator. Great care was necessary to prevent excess polymerization that results in formation of an insoluble polymer. Solvent was removed and the polymer fractionated several times to remove low molecular weight fractions. The polymers were dried and stored in the glove box. It was noted that during storage, several polymer samples became insoluble, indicating the occurrence of a reaction that leads to a higher molecular weight polymer. It is necessary to stabilize the polymer for storage or use it immediately to prepare films.

2.5. Preparation of polyvinylbenzyl ethers

Monomers were prepared by reaction of monomethyl (oligo-) ethylene glycols with vinyl benzyl chloride (Acros). Polymerization was similar to the polyacrylate ethers except that the reaction was run to only small conversions due to the high degree of cross-linking that occurred with this polymer. The molecular weights were extremely difficult to control, and soluble polymers had to be cast immediately before the material became insoluble due to cross-linking. The mechanical properties of the polymer indicated a high degree of cross-linking as the material exhibited little elasticity upon extended curing in the glove box.

3. Results and discussion

3.1. Linear polymers

The DSC analysis of pure PEMO shows a glass transition (T_g) at -60°C and a melting transition at 10°C. When lithium salts are added, the crystallinity diminishes (lower T_m and smaller ΔH_m) and with LiTFSI salts the material appears to be completely amorphous throughout the temperature range examined. The glass transition values are plotted as a function of molar concentration of the lithium salt content in Fig. 2. It should be noted that any exposure of the high salt concentration samples to atmosphere prior to measurement leads to an erroneous value of T_g, as these materials are very hygroscopic. There is a linear relationship of the T_g with the molar salt concentration, which does not appear to depend on the salt identity except at high concentrations of LiTf. At these concentrations, salt precipitation is apparent, which accounts for the deviation.

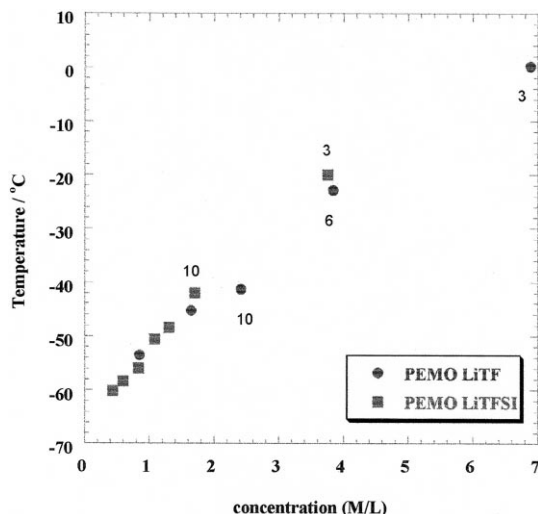Fig. 3 shows the conductivity isotherms for the two salts, LiTf and LiTFSI, in PEMO at 40°C. The LiTf salt

Fig. 2. DSC results of PEMO–LiTf and PEMO–LiTFSI. Glass transition temperatures plotted as a function of salt concentration (mol/l).

electrolyte exhibits a conductivity that is at least a half order of magnitude lower than that of the LiTFSI salt and the conductivity of the LiTf system is much more sensitive to the salt concentration. The relatively low dependence of transport properties on salt concentration is a striking feature of LiTFSI–polymer systems and was observed at all measured temperatures (40°C, 60°C and 85°C) for salt diffusion coefficients and Li$^+$ transference numbers as well as conductivities in the PEMO system. The LiTf–PEMO system exhibits a much stronger dependence of salt diffusion coefficient and transference number upon the concentration, some of which may be due to salt precipitation at high concentration. Some preliminary details of these measurements can be found in an accompanying article [10]. It is noteworthy that the superior transport properties of the LiTFSI–PEMO system are observed de-
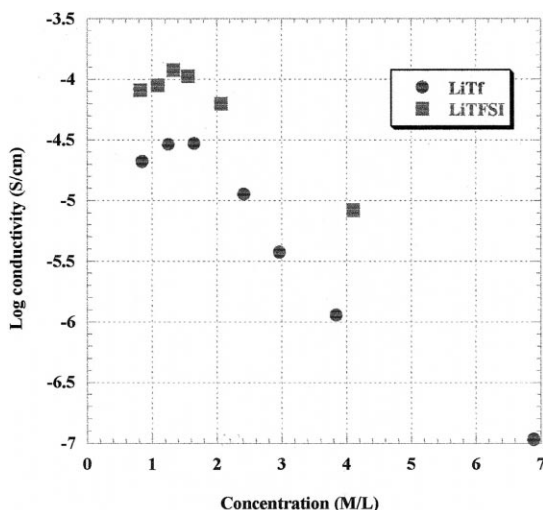
spite the similarity of the T_g behavior to that found in PEMO–LiTf. T_g values for PPO–LiTf [11] and PPO–LiTFSI [12,13] solutions are also similar to the values reported here for the PEMO analogs, but conductivities of the former are at least one order of magnitude lower [10]. The inverse correlation of T_g with conductivity does not appear to rigorously hold when the structures of the polymer electrolyte solutions are altered.

Comparison of Li$^+$ transference numbers shows that the values for LiTFSI-containing solutions are higher than for LiTf at all concentrations and temperatures of interest [10]. The measured salt diffusion coefficients of the LiTFSI salt are 3–5 times higher than LiTf salt in PEMO through a range of concentrations from 1 to 4 mol/l. It has been demonstrated that the transport properties of the salt can have profound effects upon the cycling behavior of metal oxide electrodes in sodium polymer electrolyte cells [14]. Recently, French workers have reported on the possible effect of the anion mobility on the growth of dendrites on lithium electrodes in LiTFSI–PEO solutions [15], and they account for their observations on a theoretical basis [16]. However, as the conditions examined were not exactly representative of normal battery operation (current density above the limiting current), more experimentation in this area is called for. A comparison was carried out for cycling at lithium metal electrodes. Fig. 4 shows the cycling behavior of symmetrical Li/electrolyte/Li cells at 40°C for the two electrolytes PEMO–LiTFSI (15:1) and PEMO–LiTf (20:1). The LiTFSI electrolyte has a conductivity and salt diffusion coefficient that is about five times that of the LiTf electrolyte at the concentrations used. The Li$^+$ transference number for the LiTFSI sample is 0.14, while that of LiTf is –0.14 and the dependence on concentration is much stronger for LiTf [10]. Fig. 4 shows the voltage fluctuations due to rapid formation of dendrites for LiTf under these conditions while the LiTFSI electrolyte

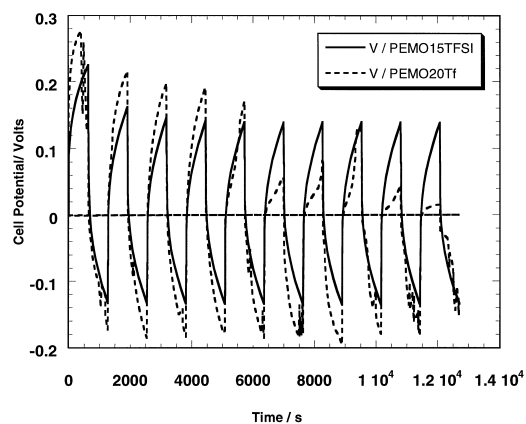Fig. 3. Conductivity of LiTf and LiTFSI in PEMO at 40°C.

Fig. 4. Cycling performance of lithium electrodes with two different polymer electrolytes in symmetrical Li/Polymer/Li cells (Current density = 0.3 mA/cm^2, Temperature = 40°C).

was cycled for hundreds of cycles before voltage variations were observed. A similar long cycle life in symmetrical lithium/lithium cells has been observed with LiTFSI with the comb branch polyepoxide ethers and polyacrylate ethers. These observations may indeed indicate an effect of transport properties on the tendency to form dendrites. However, many variables such as differing reactivity of salts and polymers at the electrodes and lower solubility limits may also be expected to play a role, not to mention the initial state of the lithium metal itself and any SEI layers that may be present. The reproducibility of these observations remains to be rigorously established before strong conclusions may be drawn regarding the role of the transport properties on dendrite growth. However, this dendrite growth represents a major performance limitation for polymer electrolytes and represents an area where much work is needed to understand the critical factors.

3.2. Comb branch polymer electrolytes

Postmortem analysis of PEMO–LiTFSI electrolytes cycled with Li_xNiO_y electrodes are reported elsewhere [17]. The degradation patterns observed at lithium electrodes are similar and both are consistent with cleavage of the polymer at the oxymethylene linkage. However, the products of reaction with the electrodes may only be interpreted in a qualitative fashion, as there may be larger fragments not detectable by the analytical method. The polymers appear to be qualitatively more liquid after cycling, indicating a decrease in molecular weight. Comb branch materials such as those shown in Fig. 1 are more amenable to chemical analysis.

Fig. 5 shows the advantages of these materials from a chemical analysis point of view, as small fragments are formed upon bond breaking, which can be analyzed quanti-
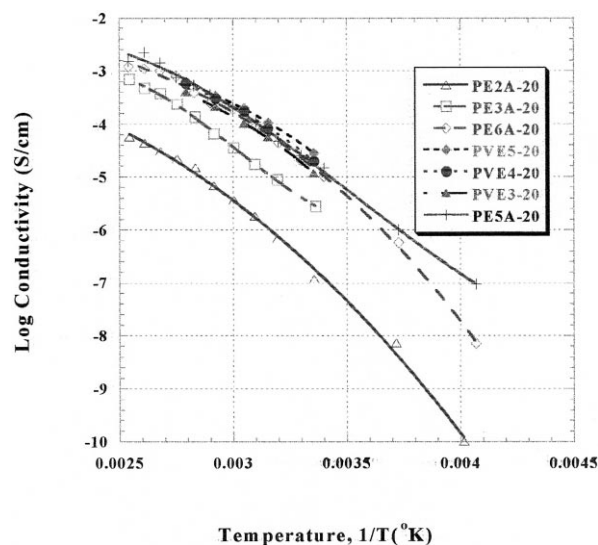
Fig. 6. Conductivities of polyacrylate ethers (PE$_x$A) and polyvinyl ethers (PVE$_x$) with LiTFSI (O/Li$^+$ = 20) as a function of temperature.

tatively by simple methods. The chemistry that is indicated here is based upon observations for cycling experiments on Li/liquid electrolyte cells [18,19]. It is assumed that, mass transport effects aside, the chemical reactivity of the oxygen–carbon bonds towards lithium metal is the same for liquids and polymers, for similar functional groups. A similar logic can be applied to reactions under oxidative conditions that occur at metal oxide electrodes. The products that are formed may be considered to play a role in the formation and operation of the interfacial protecting layers that are often described as solid electrolyte interfaces (SEI). A more important advantage of the architecture is that the structure of the side chain may be controlled precisely so that the mechanism of ion transport through the bulk and across the interfaces may be studied with respect to the polymer structure. The structure of the combs can be tailored to provide any desired reactivity or flexibility in order to test any hypothesis concerning the processes that occur at the interfaces or in the bulk of the solution. The interfacial reactivity will be reported in detail in future publications.

The synthetic strategy may involve grafting of the side chain on to a pre-formed polymer backbone such as polyphosphazene [20,21] or polymerization of pre-formed monomers [3,4,8,9,22–24]. Either approach gives rise to polymer materials with poor mechanical properties, due to the inherent shapes of the polymer chains that reduce the entanglements responsible for elastomeric strength. For practical use, the materials must be cross-linked; several approaches have been employed to achieve this [25–30]. Even though the uncross-linked materials are essentially viscous liquids, they can be studied in electrochemical cells. Conductivity data for LiTFSI-containing solutions of the polyacrylate ethers (PE$_x$A) and polyvinyl ethers
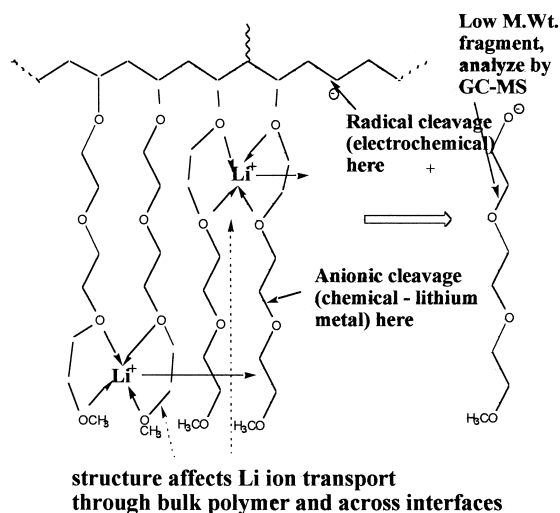

Fig. 5. Comb-branch polymer structure to illustrate how the side-chains provide information on the mechanism of ion transport through the bulk and across the electrode interfaces.

(PVE$_x$) with various side-chain lengths are shown in Fig. 6. The results for polyepoxide ethers (PEPE$_x$) of four different side chain lengths with LiTFSI are shown in Fig. 7.

VTF behavior is observed in all cases and there are distinct trends that depend on the length of the side chain and the nature of the backbone. In agreement with the literature [3,7,23], the conductivities of the PVE$_x$ and PE$_x$A materials are observed to increase with increasing side-chain length up to 5–6 EO units. Above this value, no further increase in conductivity is observed and some crystallinity is observed. The T_g values and the variation with salt concentration are also similar to that shown in Fig. 1 for PEMO. It can be seen, however, that the dependence of conductivity on the side chain length is much stronger for the PE$_x$A polymers than for the PVE$_x$ materials. This may be ascribed to less flexibility of the backbone in the former. The polyacrylate group has a more rigid structure that restricts the movement of the shorter chains. A similar dependence on side-chain length is observed with the rigid polyvinylbenzene backbone while the polyepoxide backbone appears to allow complete flexibility of all the side chain lengths (Fig. 7). This observation is consistent with the structure of the polyepoxide where a freely rotating, methylene oxide spacer group separates the ether side chains from the backbone. Although the polyepoxide backbone could play a role in ion transport, it can be noted that the backbone has a structure that mimics PPO rather than the more highly conductive PEO. It is, therefore likely that the high conductivity of the polyepoxides derives from the side chains at ambient temperatures.

Fig. 8 shows a selection of conductivity data for all the families of polymers examined here. The chain lengths are chosen to be long enough such that the effect of the
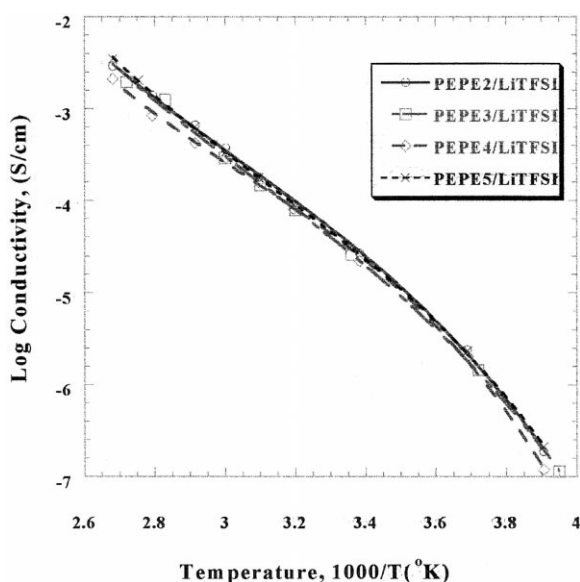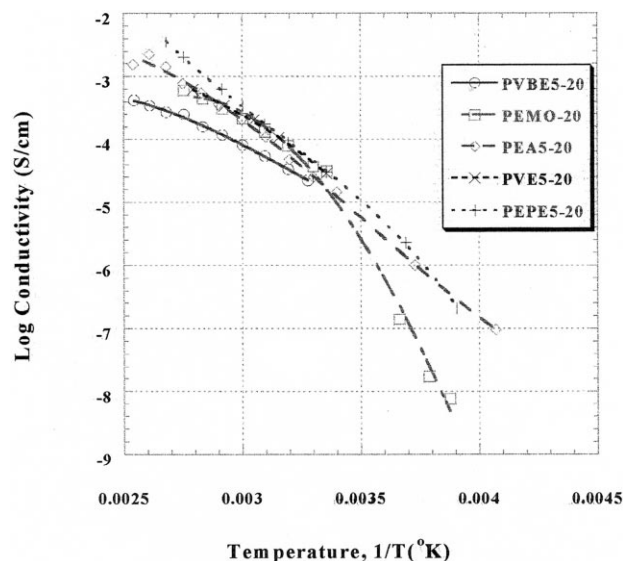

Fig. 8. Comparison of conductivities for various linear and comb branch polymers with E$_5$ chain lengths and a LiTFSI concentration of 20/1 for O/Li$^+$ ratio.

Fig. 7. Conductivity of PEPE$_x$–LiTFSI(20) as a function of temperature and side chain length.

backbone architecture on conductivity is minimized. It can be seen that all of the materials have very similar conductivities in the ambient temperature range. This observation strongly suggests the existence of a limit for materials based on ethylene oxide units for solvation of the cations. The lower conductivity of the PVBE$_5$ polymer solutions at high temperatures may be explained by the large volume occupied by the polystyrene backbone that decreases the charge carrier concentration. The very low conductivity at low temperatures for PEMO solutions suggests the presence of some crystallinity even though no melting transition is observed in DSC measurements. There may be a slow crystallization process that is only apparent after long equilibration at low temperatures, similar to what is seen in some PEO–salt systems. No evidence of crystallization is observed with the comb branch materials provided that the side chain length is less than 8 EO units.

The results are consistent with the concept that there is a limit to the conductivity of the polymer electrolytes with ethylene oxide units, even after optimization of the polymer architecture and electrolyte salt. We have found that replacement of ethylene oxide units with propylene oxide units in a polyacrylate comb branch polymer (PP$_3$A vs. PE$_3$A where P$_3$ denotes three propylene oxide units in the side chain) led to a decrease in conductivity of one order of magnitude throughout the temperature range examined ($-30°C$ to $+100°C$). These observations imply that the lithium ion may be too strongly bound to the ether oxygen for optimum mobility and that a more flexible solvating group would be kinetically more labile, leading to higher conductivities. A recent report on the conductivity of crown ethers attached to a polyphosphazene backbone [31] is also consistent with the concept of a kinetically limiting

desolvation step. The crown ether polymers exhibit reduced conductivities, presumably due to the lack of flexibility in the solvating ether groups and the chelate effect of the macrocycle.

Further conclusions on the dependence of the transport mechanisms on polymer structure await more detailed transport property measurements on the comb branch polymer to complement those already reported for the linear polymers [10]. However, the presently available results indicate that the comb branch materials will behave in a similar manner provided that the length of the EO solvating group is chosen appropriately. There appears to be a limit to the conductivity of ''dry'' polymer electrolytes that can only be overcome by changes in the structure of the solvation group unless a completely different mechanism of ion conductivity can operate (recent reports [32] indicate that this may be possible). The apparent limits for the EO-based polymer electrolytes (conductivity at 25°C = 5×10^{-5} S/cm, salt diffusion coefficient at 40°C = 8×10^{-13} m^2 s^{-1}, $t_+^o = 0.14$ at 40°C) provide little prospect of achieving viable battery performance for room temperature applications [33]. The option of addition of solvent to the polymer to increase conductivity may seriously interfere with the operation of the electrode interfaces and still does not address the issue of low transference number. The future of ambient temperature lithium-polymer batteries may thus depend upon the development of new polymer materials that:

1. Possess different solvating groups that are kinetically more labile or promote a different mechanism of ionic conduction.
2. Allow a decrease in separator thickness to less than 5 μm, which demands excellent mechanical strength while maintaining transport properties and mandates good control of the electrode interfaces.
3. Operate with added solvent, which also requires improved control of the interfaces for cycle life and safety and hence improved understanding and construction of SEI layers.
4. Have immobilized anions to give polyelectrolytes with unity transference numbers and that possess sufficient conductivity to provide a useful battery [33].

Acknowledgements

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