

Electrochemical investigation of organic salts in polymeric and liquid electrolytes

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Abstract

The electrochemical behavior of three organic bulky salts— $(\text{CF}_3\text{SO}_2)_2\text{NLi}$, $(\text{CF}_3\text{SO}_2)_2\text{CHLi}$ and $(\text{CF}_3\text{SO}_2)_3\text{CLi}$ —was investigated in an amorphous cross-linked poly(oxyethylene). The best conductivities and the lowest cationic transport numbers were found for the imide salt. Particular attention was paid to the electrochemical stability of $(\text{CF}_3\text{SO}_2)_2\text{CHLi}$ in liquid and polymer electrolytes. Compared with $(\text{CF}_3\text{SO}_2)_2\text{NLi}$, $(\text{CF}_3\text{SO}_2)_2\text{CHLi}$ was found to have a narrower stability window, both in reduction and in oxidation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer electrolyte; Lithium salts; Electrochemical stability

1. Introduction

This paper reports on a comparison of 'dry' polyether electrolytes consisting of organic salts, namely: $(\text{CF}_3\text{SO}_2)_2\text{NLi}$, LiTFSI, $(\text{CF}_3\text{SO}_2)_2\text{CHLi}$, LiTFSM and $(\text{CF}_3\text{SO}_2)_3\text{CLi}$, LiTriTFSM, in which the anions have two or three electron-withdrawing substituents. Although lithium imide LiTFSI has been widely investigated in various polymers, the di and trisubstituted carbanionic salts have not been studied to any great extent in polymer electrolytes. The selection of an appropriate host polymer is important in comparative studies. For example, linear poly(oxyethylene) are highly crystalline while amorphous poly(oxypropylene) undergo microphase separation with most of the salts [1], and due to Lewis acid traces in the salts, poly(oxyethylene) acetals undergo chemical degradation with a dramatic loss of mechanical properties [2]. In recent years, we have developed amorphous unsaturated polyethers prepared either by anionic Ring Opening Polymerization (ROP) [3] or by a polycondensation route [4]. After a free-radical initiation, both copolymers and polycondensates provide amorphous networks with a high yield in insoluble material. In addition, their mechanical properties are well-adapted to lithium polymer battery applica-

tion. Both networks provide high ionic conductivities with a slight advantage to networks originating from ROP prepolymers. Nevertheless, a random copolymerization does not provide at each synthesis copolymers with exactly the same polyether spacing between two unsaturated moieties. On the other hand, the polycondensation between poly(ethylene glycol) 1000 and 3-chloro-2-chloromethyl-1-propene, performed in alkaline medium, provides unsaturated prepolymers with a regular average spacing between two double bonds. This route provides therefore prepolymers (and then networks) with 22 oxyethylene units in average between two cross-link sites.

As compared to POE, the networks are free of any oligomer, and exhibit both a low crystallinity rate and a low melting point. In addition, they allow single-ions conductors to be prepared by copolymerization between lithium perfluorosulfonate monomers and the unsaturated prepolymers [5] during the cross-linking step.

2. Experimental

2.1. Host polymer

Unsaturated polyethers are prepared by a Williamson type polycondensation [4]. This step-growth polymerization has been performed on α,ω dihydroxyoligo(oxyethylene) $M_n = 1000$ g/mol. The polymer obtained is purified

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by ultrafiltration in order to remove any material with a molecular weight lower than 3000.

2.2. Membrane cross-linking

After casting a polymer solution in ACN including 5% in weight of a free-radical initiator, namely benzoyl peroxide, the solvent is removed without heating. Then, the films are heated at 70°C for 2 h, the thermal decomposition of the peroxide allowing the membrane cross-linking. In order to remove the soluble material (< 5% in weight), the membranes are swollen and washed in a large excess of methanol. After the methanol removal, the different salts are incorporated by swelling the membrane with an ACN salt solution. After the ACN removal, the weight difference between the membrane electrolyte and the membrane free of salt provides the electrolyte composition. In this way, the membrane is fully cross-linked and free of any low molecular weight polymer.

2.3. Synthesis of ammonium salt

In order to prepare the tetraethylammonium salt of TFSM (AmTFSM) the acidic form of the salt, i.e., HTFSM, has been treated by a stoichiometric amount of hydroxytetraethylammonium (Aldrich). HTFSM, obtained from Hydro-Quebec, is beforehand submitted to sublimation. AmTFSM is then dried in vacuum for several days at a temperature close to 30°C, to prevent the ammonium degradation.

2.4. Thermal analysis

Glass transition temperatures, T_g , and melting temperatures, T_m , are measured in helium using a Netzsch STA409 Thermal analyser. The analyses were performed in the temperature range 100°C–150°C, with a heat rate of 10°C min⁻¹.

2.5. Ionic conductivity

The ionic conductivities of the lithium salt/polymer complexes were determined, under dynamic vacuum, by impedance spectroscopy over the frequency range 5 Hz–13 MHz, using stainless-steel blocking electrodes and a HP 4192A analyzer.

2.6. Transport number

The transport number determinations have been performed by a combination of complex impedance and potentiostatic polarization measurements. The sample is sandwiched between two metallic lithium electrodes [6]. The polarization voltage is kept at 10 mV using a Mac Pile computer device, providing an accuracy of 0.25 μ A and 1.25 mV on intensity and voltage, respectively.

2.7. Cyclic voltammetry

2.7.1. Polymer electrolytes

The voltammetry is performed using a three-electrode configuration cell. Stainless-steel is used as working electrode while two lithium metallic foils are used as reference and auxiliary electrodes. The experiments are carried under dynamic vacuum with a scanning rate of 7.5 mV/min with a Mac Pile computer device.

2.7.2. Liquid organic electrolytes

The investigation on the reduction stability of LiTFSM solutions in ethylene glycol dimethylether has been performed, using a two-electrode configuration cell with a copper microelectrode ($\phi = 100 \mu\text{m}$). The experiments have been carried out in a glove box in argon with a 5 mV/s scan rate.

The limiting reduction and oxidation potentials of the quaternary ammonium TFSM have been evidenced in propylene carbonate (PC) using either a glassy carbon or platinum as working electrodes, at a 5 mV s⁻¹ sweep rate. A 0.3 mol l⁻¹ electrolyte concentration has been used. The experiments have been performed, in glove box, using a double junction reference electrode of Ag/Ag⁺ and a glassy carbon as auxiliary electrode. Prior to each scan, the working electrodes are polished. The limiting reduction and oxidation potentials are taken at the onset of the wave.

3. Results and discussion

3.1. Ionic conductivities

The comparison of the ionic behaviour of LiTFSI, LiTFSM and LiTriTFSM has been performed in NPC1000 host polymer. Classical Arrhenius plots of NPC1000/LiTFSM electrolytes are compared in a wide range of concentration (Fig. 1). The best conductivities, i.e., $6.5 \cdot 10^{-6}$ S/cm at 20°C and $4 \cdot 10^{-4}$ S/cm at 84°C, have been reached for a rather low salt concentration O/Li = 19. Due to the amorphous character of the network, the room temperature conductivity is higher than that previously reported by Benrabah et al. [7] in high molecular weight POE. Yet, these authors observed slightly higher conductivities at high temperature, with $6.5 \cdot 10^{-4}$ S/cm at 75°C. Taking into account that our network is free of any oligomeric chains the results are in good agreement. On the other hand, Holcomb et al. [8] reported in POE higher conductivities for the composition O/Li = 16 in the whole temperature range with $2 \cdot 10^{-5}$ S/cm at 20°C and $1.5 \cdot 10^{-3}$ S/cm at 80°C, but their sample underwent a preliminary thermal treatment.

In LiTriTFSM, often called methide, the bulky carbanion is substituted by three electron-withdrawing groups. The third substitution is expected to improve the negative charge delocalization, the ion-pair dissociation and the electrochemical stability in oxidation. Arrhenius plots of

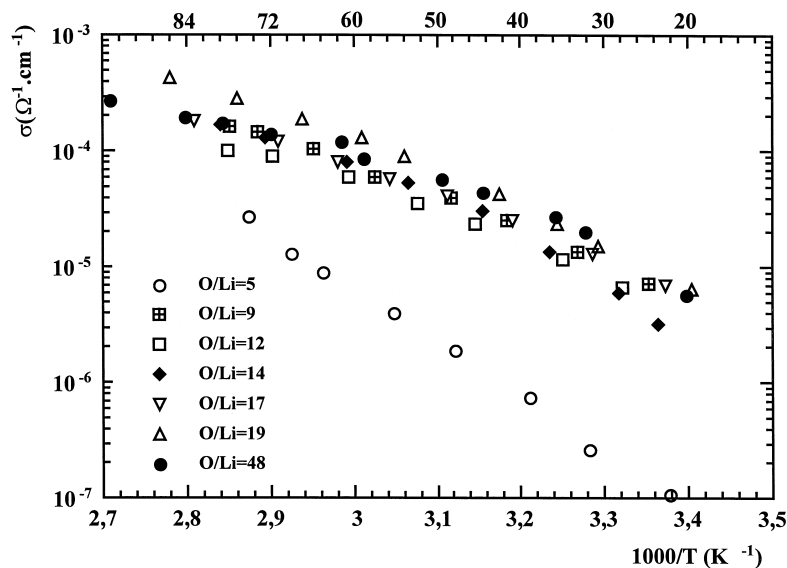


Fig. 1. Conductivities vs. T^{-1} for NPC 1000/LiTFSM electrolytes at various salt concentrations.

NPC1000/LiTriTFSM electrolytes are compared in a wide range of concentration (Fig. 2). The best conductivities, obtained for O/Li = 16.5, are very close to that obtained with LiTFSM reaching $4 \cdot 10^{-6}$ S/cm at 20°C and $3 \cdot 10^{-4}$ at 80°C. On the other hand, poor conductivity values were obtained at high salt concentration. These values are surprisingly lower than that reported by Benrabah et al. [9] in POE. The electrolyte conductivities exhibit a free-volume behaviour typical of amorphous complexes, in accordance with DSC analyses. Fig. 3 provides a comparison of the Arrhenius plot for these two salts complexes with LiTFSI/NPC1000 electrolytes. This last electrolyte presents the best conduction behaviour, five times higher in

all the temperature range than thus noted with these carbanionic salts. In addition, the latter are also less conductive than usual salts such as lithium perchlorate [4] or lithium iodide [10] which performances are very close to that of LiTFSI in the same NPC1000 networks. The lower conductivities of the carbanionic salts may be related to the ion-pair dissociation, i.e., the concentration in charge carriers, or a lower anionic conductivity. Indeed, a comparative *ab initio* investigation [11,12] performed on TFSI⁻, TFSM⁻ and triflate Tf⁻ revealed that both TFSI⁻ and TFSM⁻ show roughly the same delocalization of the negative charge with a slight advantage for the imide anion. For methide anion we may expect, from the third

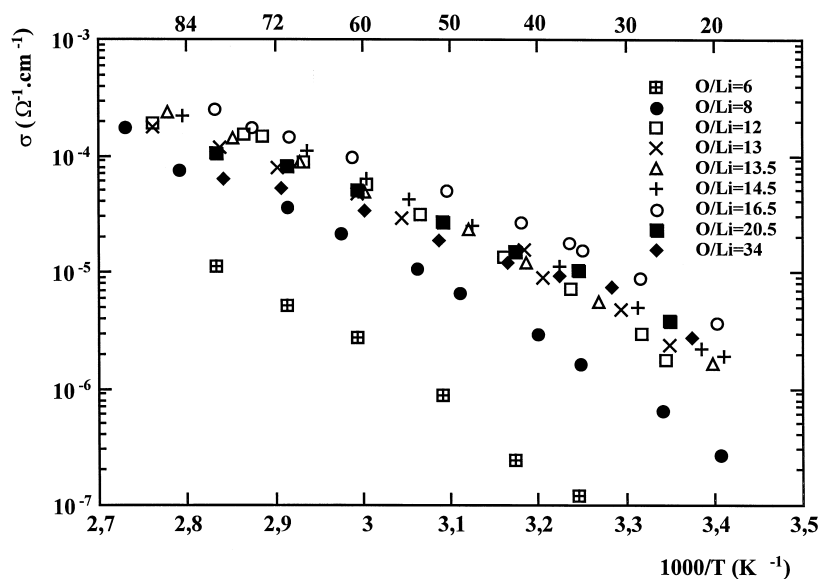


Fig. 2. Conductivities vs. T^{-1} for NPC 1000/LiTriTFSM electrolytes at various salt concentrations.

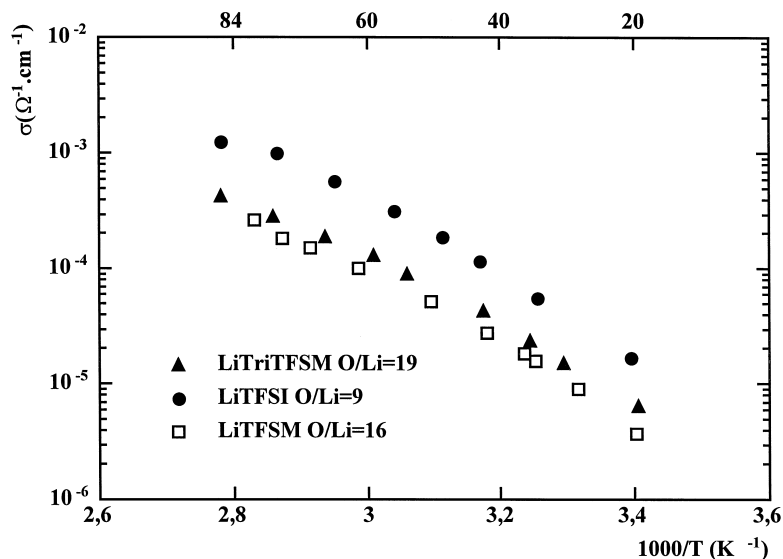


Fig. 3. Comparison between the best conductivities vs. T^{-1} of NPC 1000 electrolytes.

electron-withdrawing substituent, an extension of the delocalization or at least the same delocalization level than in TFSI⁻ and TFMS⁻. As for the ionic character of the three salts an ab initio investigation performed on LiTFSM and LiTFSI ion-pairs have shown the same form of lithium cation ‘chelation’ and the same percentage of covalent bonding in gas phase for both salts [13]. The dependence of ionic mobility on the segmental mobility of the polymer is well-known in polyethers free of solvents or oligomeric materials and is classically evidenced by the T_g s evolution with the salt concentration, i.e., by plotting T_g s vs. the salt concentration, expressed in O/Li. Fig. 4 provides a comparison of the T_g s between these three salts. If the slope

$\delta T_g / \delta(O/Li)$ are very close for the different electrolytes, LiTriTFSM exhibits the highest T_g s, while the T_g s are roughly the same for LiTFSM and LiTFSI electrolytes. This result may explain the discrepancy observed between the conductivities of LiTriTFSM in NPC1000 networks and those previously reported [9] in POE. Indeed higher conductivities were reported in linear POE but with lower T_g s than NPC1000/LiTriTFSM ones. In order to appreciate the effect of the segmental mobility on the conductivities in NPC1000 host polymer, the conductivity dependence with temperature, at the same reduced temperature $T - (T_g - 25)$, has been plotted (Fig. 5) for the best electrolytes. Even at reduced temperature, LiTFSI provides the

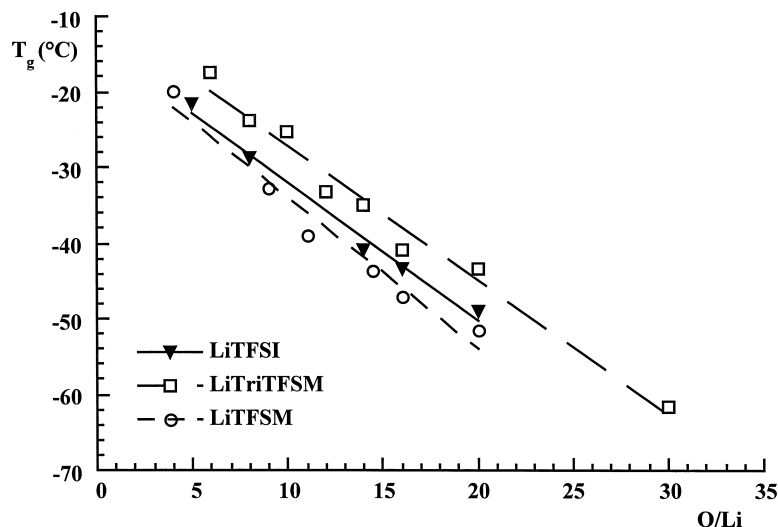


Fig. 4. T_g vs. O/Li. Influence of salt concentration on T_g s for NPC 1000 electrolytes.

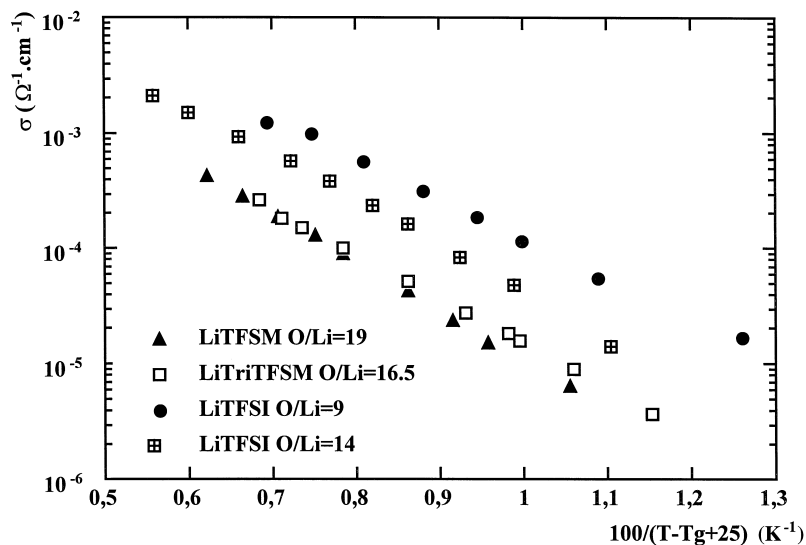


Fig. 5. Conductivities vs. (reduced temperatures)⁻¹ of the best conductive NPC 1000 electrolytes.

highest conductivities. This may be connected to the anion flexibility in agreement with the theoretical calculations performed by Arnaud et al. [13]. Indeed, the conformational analyses of TFSI⁻ and TFSM⁻ have shown that both anions are flexible but that the energy barrier of TFSI⁻ #5 KJ/mole is about 10 times lower than that of TFSM⁻ close #50 KJ/mole. Two concentrations, O/Li = 9 and O/Li = 14, have been plotted for LiTFSI as their conductivities are very close. Although at high salt concentration, the conductivities are clearly higher for LiTFSI, in the range of medium concentration and at reduced temperature, they are closer. This kind of comparison is useful for a better understanding of the conduction mechanism but obviously from a practical point of view the conductivities

must be appreciated not at reduced temperature but at a given temperature. On the other hand, cationic transport number is probably a more important parameter to appreciate the potentiality of a salt.

The cationic transport number t_{Li+} evolutions with the salt concentration, at 80°C, have been plotted for these three salts (Fig. 6). Some of these values were partially reported [14] but the study has been extended to TFSM and transport numbers were determined at different concentrations. Our values are very close, for LiTFSI, to that early reported by Watanabe and Nishimoto [15] in other amorphous cross-linked polyethers. All these salts show a prevalent anionic transport as t_{Li+} does not exceed 0.2, the lowest values being obtained with LiTFSI and the

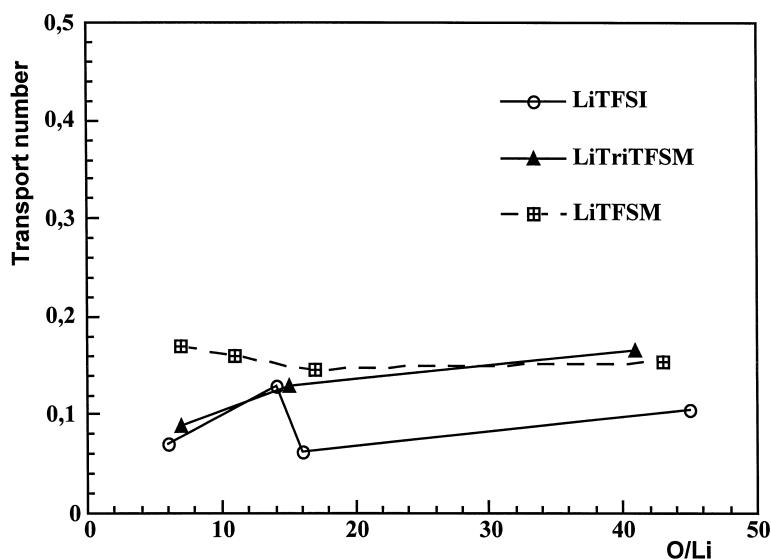


Fig. 6. Lithium transport number in several NPC1000 salt complexes.

highest for LiTFSM, while the values for LiTriTFSM range between 0.09 and 0.16. From that results we may infer that the anion bulkiness does not influence the anionic motion in this kind of salts. Coming back to the transport number of LiTriTFSM, our value is lower than that determined by Dominey et al. [16], $t_{Li^+} = 0.33$ for MEEP/LiTriTFSM complexes. But of course, the solvating ability of polyether blocks towards lithium cation is probably higher than that of the small dimeric ethers of MEEP which is a comb polymer, polybis(methoxyethoxyethoxyphosphazene), and may reduce the lithium mobility as compared to MEEP. This difference in solvating properties may explain the discrepancy with the previous paper.

3.2. Electrochemical stability investigation

Impedance analyses of symmetrical cells Li–electrolyte–Li have been performed to compare the interface resistance of polymer electrolytes prepared by dissolution of these three salts in NPC 1000. The semi-circle observed at middle frequencies is related to interface passive film. The cells have been stored and tested in dynamic vacuum and under open circuit conditions at 80°C. From this comparative study (Fig. 7), it appears clearly than the interface resistance is markedly higher in NPC1000/LiTFSM electrolytes. Although it may be noticed that this resistance decreases with time. The decrease of the interfacial resistance of Li/LiTFSM electrolyte may be related to an instability of the passivation film in a solvating polymer. The latter is probably connected to a dissolution of the film in the polyether network. As the kinetics of the reactions are slow in polymeric solvents, further investigations will be carried out using oligomeric polyethers.

Whatever the causes of the interfacial resistance decrease, LiTFSM electrolyte appears less stable in reduction than LiTFSI and LiTriTFSM ones.

As a matter of fact, LiTFSM owns a remaining labile proton on the secondary carbanion. Thus, both protons of the acidic form HTFSM are easily removed when reacting 1 mole of the latter with 2 moles of an organomagnesium compound. In addition, ab initio calculations performed on the anion and the ion-pair [11–13] have allowed the charge density to be calculated and have provided positive values of respectively +0.30 and +0.32 electrons on the hydrogen atom. If none of the usual salts are thermodynamically stable vs. metallic lithium, LiTFSM should be thermodynamically still more unstable vs. metallic lithium, giving rise to an electrochemical instability in reduction. Lastly, the previous reports are evidenced by cyclic voltammetry, a complete instability of this salt. The cyclic voltammeteries were either performed on copper microelectrodes or on platinum macroelectrode [17]. More recently, opposite results were published [8]. In order to elucidate this point, we have performed a comparative investigation of LiTFSI and LiTFSM by cyclic voltammetry, in liquid as well as in polymer electrolyte.

The cyclic voltammetry performed on NPC1000/LiTFSM (O/Li = 12) electrolyte at 80°C, over a potential range from -0.1 to 4 V vs. Li/Li⁺ with a stainless-steel as working electrode, is reported in Fig. 8 and shows a small peak in reduction close to 1.5 V vs. Li/Li⁺. The latter is probably due to reduction of water traces. A rather good stability in reduction is observed, although the lithium plating-stripping affords only a yield close to 50%. As the conductivities are lower in polymer electrolytes than in liquid electrolytes, a possible instability is more difficult to evidence. So, in order to accelerate an eventual reactivity of LiTFSM, we selected to perform the cyclic voltam-

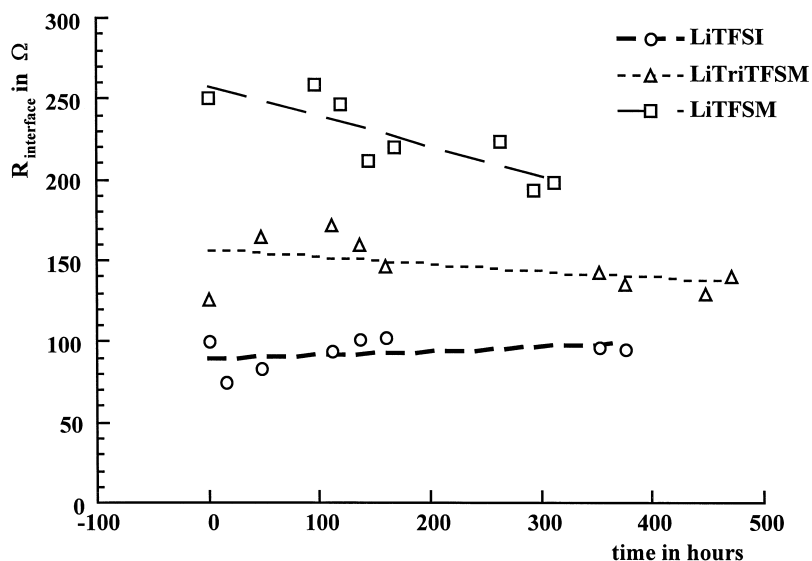


Fig. 7. Evolution of interface resistance for polymer electrolytes based on the three salts.

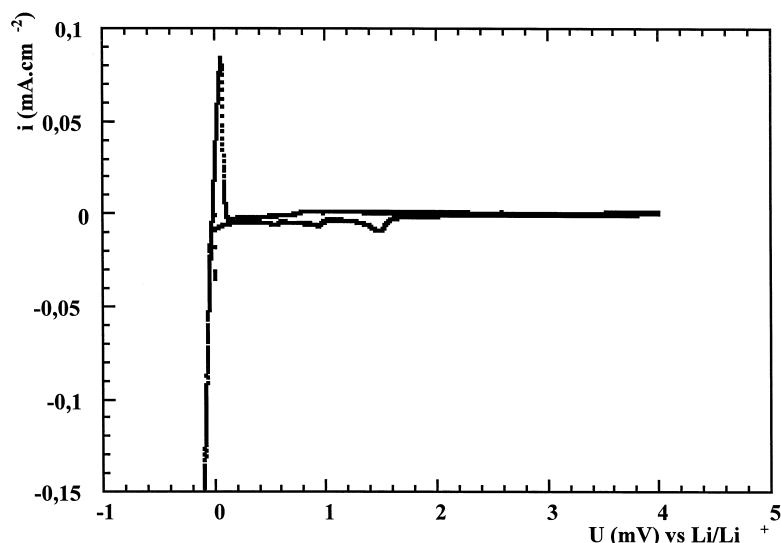


Fig. 8. Cyclic voltammetry of NPC1000/LiTFSM on stainless steel macroelectrode, performed at 80°C, sweep rate 5 mV/min.

metry in liquid ethylene glycol dimethylether, used as a liquid model of end-capped polyethers. The kinetics of the lithium deposition-stripping process have been investigated using progressive time interval between lithium deposition, on a working copper electrode, and anodic stripping. The deposition/stripping yield plotted in Fig. 9 as a function of the square root of the contact time between the electrolyte and the lithium deposit, \sqrt{t} , is linear for LiTFSI and LiTFSM electrolytes. The amount of lithium consumed during the formation of the passivation film evolves therefore with \sqrt{t} as the reaction is limited by a diffusion process of the electrolyte through the passivation film [18]. The initial yield ($t = 0$) is lower with LiTFSM electrolyte than with LiTFSI one, 68% against 90%, respectively. In

addition, the slope of the straight is about twice higher in LiTFSM electrolyte than in LiTFSI electrolyte. Taking into account that the conductivities of these liquid electrolytes are very close, it may be assumed from the slope difference, that the electrolyte diffusion through the passivation film is faster with LiTFSM. That might be related to the nature of the passivation film (composition, solubility, porosity, etc.). Lastly, we must emphasize that only 20% of lithium deposit is oxidized after 2 h on surrender potential for LiTFSM electrolyte, as compared to more than 60% for LiTFSI one. From this preliminary study, LiTFSM appears less stable in reduction than LiTFSI.

To prevent a lithium deposit which can masked other reduction reactions, we synthesized tetraethylammonium

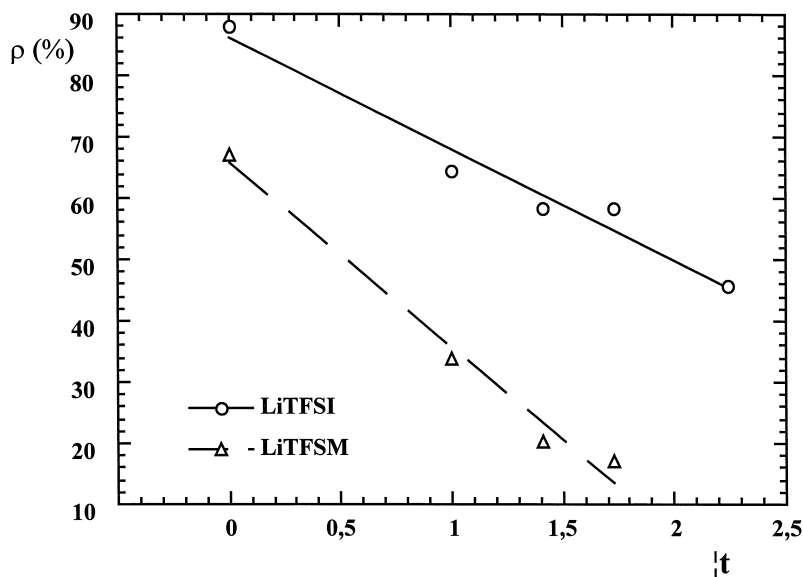


Fig. 9. Evolution of faradaic yield vs. (contact time)^{0.5} between lithium and electrolyte.

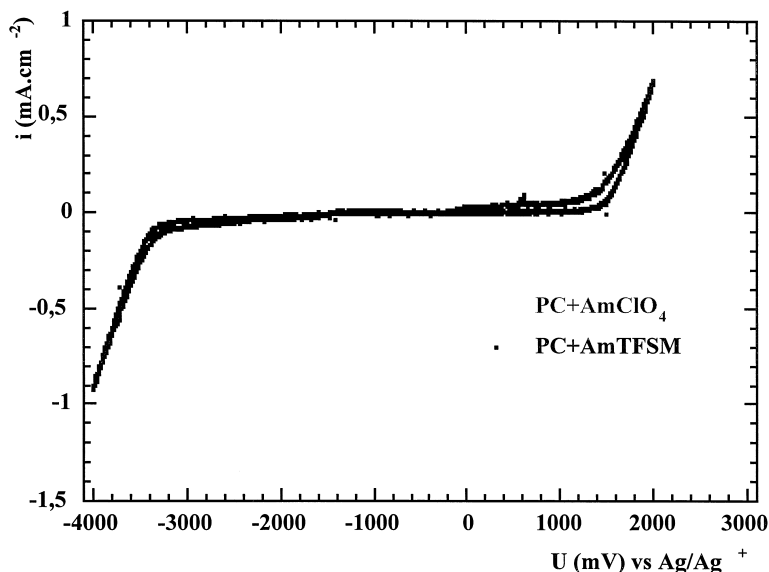


Fig. 10. Cyclic voltammetry comparison of propylene carbonate solutions of AmClO₄ and AmTFSM, performed at room temperature on glassy carbon macroelectrodes, sweep rate: 5 mV/s.

TFSM (AmTFSM), and investigated its limiting reduction and oxidation potentials on a glassy carbon, electrode which is not-limiting in oxidation. Due to its wide electrochemical stability window [19], propylene carbonate has been selected as solvent. The AmTFSM has exhibited a good stability in reduction but also an oxidation wall starting at 1.5 V vs. Ag/Ag⁺ (i.e., 4.8 V vs. Li/Li⁺) [20] (Fig. 10), namely 0.5 V lower than that observed with AmClO₄ in the same condition, the perchlorate anion itself being less stable in oxidation than most of the anions of superacids (PF₆⁻, SbF₆⁻, AsF₆⁻, BF₄⁻) [19]. To investigate the stability in reduction accurately, the cyclic voltam-

try of the same electrolyte has been performed using a platinum macroelectrode as working electrode (Fig. 11). If the cyclic voltammetry begins by a scan in oxidation, up to 1.1 V vs. Ag/Ag⁺, no peak is detected during the first scan, in accordance with the previous observations on glassy carbon. On the other hand, during the reduction scan, stopped before the solvent reduction, a peak, which may be due to the reduction of the remaining proton of TFSM, starts at -2.1 V vs. Ag/Ag⁺ (+1.2 V vs. Li/Li⁺). For this reason, the second scan in oxidation exhibits two peaks around -0.2 V vs. Ag/Ag⁺ (+3.1 V vs. Li/Li⁺). Benrabah et al. [17] reported cyclic voltam-

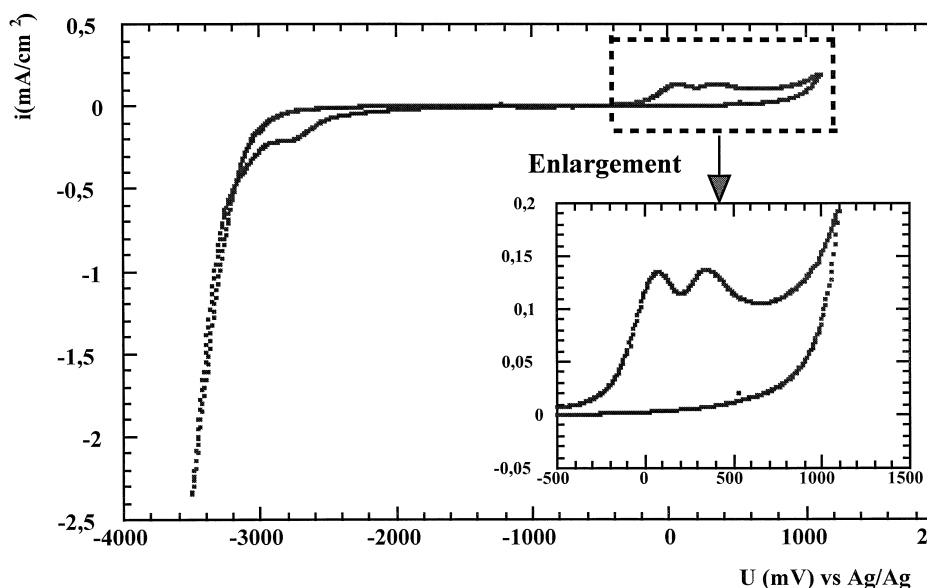


Fig. 11. Cyclic voltammetry of propylene carbonate solution of AmTFSM, performed at room temperature on platinum macroelectrode, sweep rate: 5 mV/s.

metries performed on LiTFSM/POE complexes, using platinum electrode which exhibits a similar behaviour and have assigned the peak observed during the oxidation scan to the oxidation of hydrogen formed during the reduction scan by the reduction of the remaining hydrogen of TFMS.

4. Conclusion

The cross-linked polyether selected as host polymer, may be used as a model host polymer, well-adapted to compare the salts, from ambient temperature, in a wide concentration range. The conductivity comparison between the three salts in this network has shown that the maxima are close for the two carbanionic salts. But, at least two compositions in LiTFSI provide higher conductivities, above all at high salt concentration. In these polyethers, free of any oligomers or non cross-linked chains, the anionic conductivity is prevalent above all for imide and methide salts. The electrochemical study, mainly focused on a comparison of LiTFSI and LiTFSM confirms the lower stability, both in reduction and oxidation, of LiTFSM. Nevertheless, this study must be followed by battery tests, using NPC 1000 as host polymer.

Acknowledgements

This work has been carried out with the financial support of Hydro-Quebec.

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