

Polymer and salt selection for lithium polymer batteries

J.-Y. Sanchez ^{a,*}, F. Alloin ^a, D. Benrabah ^a, R. Arnaud ^b

^a LEPMI, Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces, Domaine Universitaire, BP 75, 38402 Saint-Martin-d'Hères Cedex, France

^b LEDSS, Université Joseph Fourier, Domaine Universitaire, BP 53, 38041 Grenoble Cedex 9, France

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Abstract

Several network-based polymer electrolytes provide both thermal, mechanical and redox stabilities, while insuring a high conductivity level. Linear unsaturated polyether precursors may be obtained either by step-growth polymerization from oligomeric polyethers or by ring-opening polymerization from oxirane mixtures. In addition, theoretical investigations on several lithium salts are presented, which allowed optimized geometries as well as charge densities to be established in the gas phase. © 1997 Elsevier Science S.A.

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1. Introduction

This last decade a growing interest has arisen in polymer electrolyte based batteries. At this stage, we must differentiate all-solid polymer electrolytes and plasticized polymer electrolytes. The latter, notably polyvinyl acetals swollen by organic solvents, such as propylene carbonate, were first proposed by Feuillade et al. [1]. The incorporation of solvent decreases the glass transition but, at present, it is not clear whether the conductivity increase at ambient temperature is in relation with the increase in chain mobility or the increase in dielectric constant, as most of the solvents used exhibit a high dielectric constant. In spite of the interest of such systems for low temperature applications, these kinds of plasticizers exhibit the same behaviour as in liquid electrolytes and most of them are unstable with metallic lithium. We focus our presentation, therefore, on non-plasticized polymer electrolytes, i.e. polymer/salt complexes. Although recently introduced in the electrochemical sciences [2] the knowledge of polymer/salt complexes started in the beginning of the 1960s, with the report by Blumberg et al. [3] on poly(oxyethylene) (POE)/HgCl₂ complexes followed by the paper by Moacanin and Cuddihy [4] on the poly(oxypropylene)/LiClO₄ complexes. Already, these reports showed the dramatic T_g increase with the addition of salt. Later, in 1973, Fenton et

al. [5] revealed the conductivity of POE-based complexes of NaI, NaSCN and KSCN and its relation with the fusion of the crystalline phase. Although it may be artificial to separate salts from polymers, as the nature of the anion may completely modify the salt/host polymer interaction, we have selected, for convenience, to treat separately the two constituents of the polymer electrolyte. A first part will be devoted to the tailoring of host polymers, including the influence of polymer architecture on the ionic conductivity of polymer electrolytes. In contrast to this applied approach, organic lithium salts will be presented in light of ab initio calculations.

2. Polymer electrolytes

2.1. Design of the host polymer

A polymer electrolyte has two functions: that of separator and of solid organic solvent. It must therefore meet the following requirements to be used in lithium batteries:

1. electrochemical stability towards metallic lithium but also towards cathode materials in order to avoid the increase of the interfacial resistance which affects the battery performance and shortens its lifetime;
2. high ionic conductivity at the operating temperatures of the batteries;
3. high thermal stability, notably at temperatures above 200°C, and

* Corresponding author.

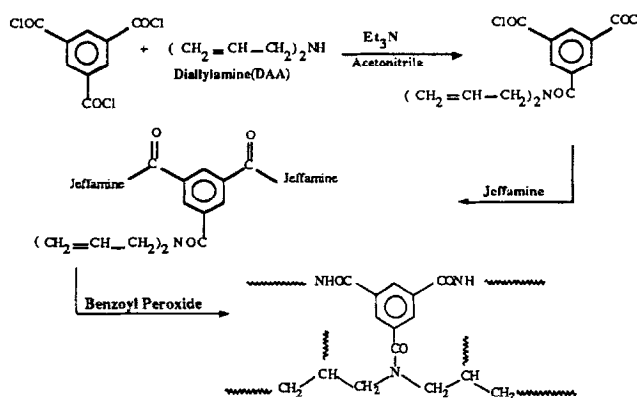
4. high mechanical stability in order to lower the electrolyte film thickness, thus minimizing the ohmic drop in the polymer electrolyte, while avoiding the risk of a short-circuit.

The specifications of electrochemical stability exclude the use of most of the protic groups which react with metallic lithium, generating hydrogen. Most of the labile or acidic protons must, therefore, be avoided, i.e. carboxylic acids, alcohol, primary amide, urethane, and even primary or secondary amines. The 'acceptor number' (AN), high in protic solvents which enable an efficient solubility of the anions through hydrogen bonds, will be low in host polymers selected for lithium batteries. Thus, the main driving force for salt solubility remains the high polymer donicity (high 'donor number') which allows a strong Li^+ /electron pair interaction. This great ability to dissolve the lithium cation, through electron-donating atoms, may be found in polymers stable with metallic lithium such as polyethers, or tertiary polyamines. However, polyamines have a rather limited stability towards oxidation. Polyethers appear therefore as the best candidates for lithium battery applications. Among these polyethers, poly(oxyethylene) (POE) are preferred, as they allow a better solubility of alkaline, as well as divalent and trivalent salts. It is generally admitted that among the polyethers the oxyethylene repeat unit is the most favourable to salt dissolution. The use of linear high molecular weight POE is an advantage as the polymer is perfectly soluble, commercially available, can be melted and might be recycled. Owing to the long range regularity and the absence of branching, POE homopolymers have high crystallinity which, due to the chain entanglements, is decreased in high polymers but still remains close to 70%. Nevertheless, new lithium salts allow the decrease of the melting point leading to amorphous POE-based electrolytes at ambient temperature. The polymer electrolyte however does not benefit, at the battery operating temperature, from the mechanical strength provided by the crystalline phase and may show a tendency to creep. Furthermore, thermal or chemical degradation processes of any unidimensional high polymers, shorten the macromolecular chains, decrease the chain entanglements and affect drastically its mechanical properties.

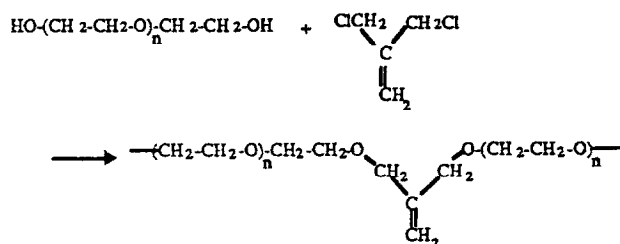
Taking into account all the previous requirements, we have selected as host polymers, two kinds of three-dimensional polyether. This approach has already been proposed by Cheradame and Le Nest [6] who studied model networks mainly based on three-dimensional polyethers cross-linked by urethane bonds. These model cross-linked electrolytes enabled them to investigate the mechanisms of ionic conductivity in polymer electrolytes. In the case of polyurethane networks, however, the cross-linking originates from the condensation reaction between alcohols and isocyanate groups, both unstable versus metallic lithium. In such a reaction, the conversion rate decreases with the dramatic viscosity increase and there may remain, in particular at an industrial scale, residual unreacted groups such as primary alcohol and isocyanate functions. Obviously at the laboratory scale, the membrane

must be free of these functions. In order to avoid the presence of residual functions, very sensitive to lithium metal, we selected to prepare unsaturated polycondensates or unsaturated copolyethers. In these prepolymers cross-linking is achieved by free-radical initiation of the vinylic or allylic moieties. In the same way as for polyurethane networks the viscosity increase is detrimental to the reaction yield, and unreacted double bonds remain in the network. But their sensitivity versus reduction or oxidation is by far lower than that of functional groups used in step-growth reaction.

Thus polycondensation of α,ω -diamine poly(oxyethylene) with an unsaturated dihalide dicarboxylic moiety provides an unsaturated polyether [7] which can be cross-linked by free-radical initiators in a second stage, according to the following scheme:



Although the amide bond is sensitive to lithium metal, its concentration is low. Moreover, the use of a secondary amine, providing a secondary amide, should enable the redox instability to be overcome. Another way to prepare unsaturated polyether by polycondensation consists in a simple Williamson-type synthesis [8] between α,ω -dihydroxypoly(oxyethylene), namely PEG, and a dichloroisobutenyl moiety according to the following reaction



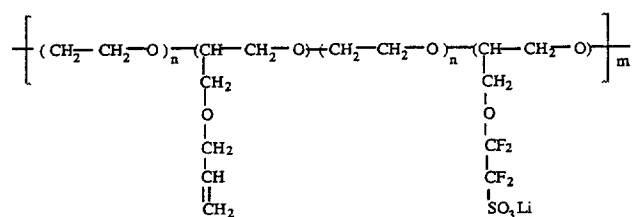
This step-growth polymerization has been performed on a wide variety of starting PEGs: PEG 400, 1000, 1500, 3400, 4600. According to the length of the starting PEG, the double bond spacing is modified while the cross-link density decreases with the spacing increase. Due to the equireactivity of OH terminal groups, polycondensates may be prepared from a mixture of oligomers. As previously reported, the

disorder induced by the presence of different spacing in the same linear polycondensate decreases both the melting point and the crystallinity content. Alternatively, mixing of different homopolycondensates, i.e. with the same spacing between two isobutenyl functions, provides a compatible blend resulting, after free-radical cross-linking of the double bonds, in a compatible interpenetrated network. According to the starting PEGs the disorder, induced in copolycondensates by the presence of different spacing in the same macromolecular chain, is generally more efficient than that induced by blending different homopolycondensates, taking into account the evolution of the melting point, see Table 1.

This step-growth polymerization may be extended to a wide variety of α,ω -dihydroxy oligomers such as poly-(tetrahydrofuran) or poly(oxypropylene) (POP). Nevertheless, the reactivity of terminal OH depending on the alcohol class (primary or secondary) as well as the location of the penultimate oxygen atom may affect the effectiveness of the reaction.

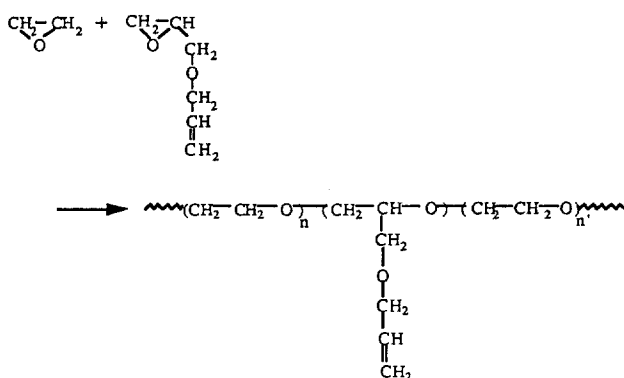
This convenient synthetic way allows the polymer architecture to be tailored, modifying crystallinity, melting point and solubility properties according to the polymer electrolyte specifications. A wide range of starting PEGs, PPGs and PTHFs are commercially available. However, due to difficulties of organic synthesis, the dihalide compound is expensive and this may have repercussions on the price of the polymer.

Another way to prepare polyethers consists in the ionic polymerization of oxiranes. These undergo a ring-opening polymerization which may be initiated by cationic, anionic or coordination catalysts. Due to its low boiling point ($T_b = 14^\circ\text{C}$), inflammability and vapour-explosive character, the handling of ethylene oxide monomer requires a high-pressure reactor vessel, while the reaction must be performed in an explosion-proof, well-ventilated hood. Ionic polymerization allows the synthesis of appropriate tailored copolymers. As an example the following terpolymer was prepared from a mixture of three oxiranes using Vandenberg-type catalyst



Crystallinity and melting point of the resulting terpolymer are markedly decreased, as compared with those of high molecular weight POEs, the allylic double bonds allowing later cross-linking while the perfluorosulfonated oxirane unit induces an exclusive cationic transport.

Except for a specific purpose such as the synthesis of a single cation-conductor network we selected bipolymers rather than terpolymers, since the reaction depends only on two reactivity ratios as compared to six reactivity ratios which govern the terpolymerization. Thus unsaturated bipolymers were prepared from ethylene oxide (EO)/allyl glycidyl ether (AGE) mixtures [9] according to



using either Vandenberg-type catalysts based on trialkylaluminum or alkoxides such as potassium tert-butoxide. If the former type, catalysts provide very high molecular weight polyethers, the double bond distribution is heterogeneous, and the impact of AGE units on crystallinity and melting point is therefore rather limited. Conversely, anionic polymerization allows one to get a statistical distribution of AGE units in the EO/AGE bipolymer. Thus, the melting points of the different EO/AGE bipolymers are very close that those of PEG oligomers corresponding to the ideal spacing (calculated from EO/AGE molar ratio) between two AGE units.

In both polycondensates and copolymers the unsaturated moieties provide three main functions:

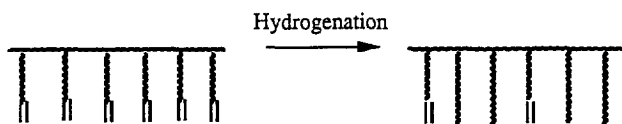
1. disrupting the long range order, they decrease the crystallinity content as well as the melting point of the host polymer;
2. allowing the polyether cross-linking, they improve the mechanical properties and still decrease the melting point as compared to the linear material, and
3. allowing single-cation conductors to be obtained, using monomers with an ionophoretic function.

Table 1

Melting point ($^\circ\text{C}$) of linear polycondensate (LPC) according to the oligomer spacing. LPC400-1000: different spacing in the same polycondensate. Blend LPC400/LPC1000: blending of polycondensates LPC400 and LPC1000

% of PEG400	0	25	50	75	100
T_m of LPC400-1000	33	32	28	16	-8
T_m of LPC400-3400	45	45	44	42	-8
T_m of blend LPC400/LPC1000				32	
T_m of blend LPC400/LPC3400		47			

In some cases, in order to get amorphous polyethers at a very low temperature, the increase in unsaturated moiety results in an increase of the cross-link density, and the conductivity drops. In order to avoid copolymerization involving three monomer units, we selected a polymer modification by a hydrogenation process, which converts the previous bipolymer into a terpolymer [10]



This simple process, well-adapted to industrial scale-up, which may also be applied to the previous polycondensates, allows the crystallinity to be greatly reduced without increasing the cross-link density.

2.2. Thermal and mechanical stability

2.2.1. Thermal stability

Fig. 1 gives the temperature and cell voltage evolution after a short-circuit test performed on a 10 Wh cell [11]. The left curve shows the dramatic voltage decrease from about 3 V while the bold curve represents the cell temperature which increases from 60 to 190 °C within ~50 min. At this temperature, the metallic lithium is melted, no exothermal reaction occurring. The absence of low boiling point products insures a high safety level for lithium polymer batteries. In order to check the stability of our network electrolytes we have performed thermogravimetric analysis (TGA) on a cross-linked polycondensate 1000, LiTFSI, NPC 1000, LiTFSI electrolyte. At 250 °C in helium, no weight loss was observed after 12 h. On the contrary, heating the same sample, in air, for 10 h at 190 °C resulted in an average weight loss close to 3.5% per hour (Fig. 2). From TGA performed on

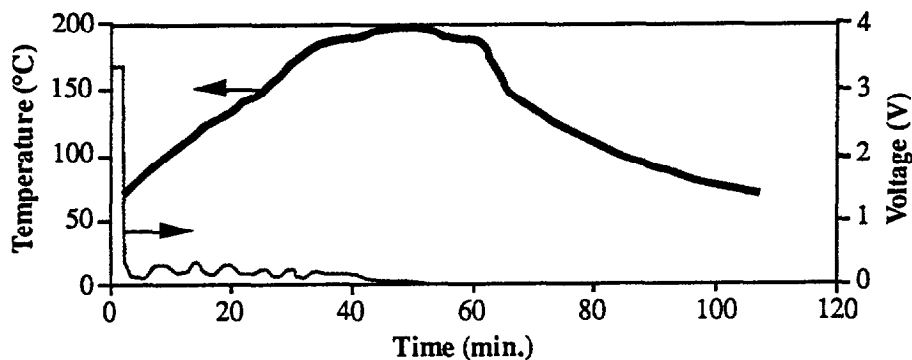


Fig. 1. Short-circuit test.

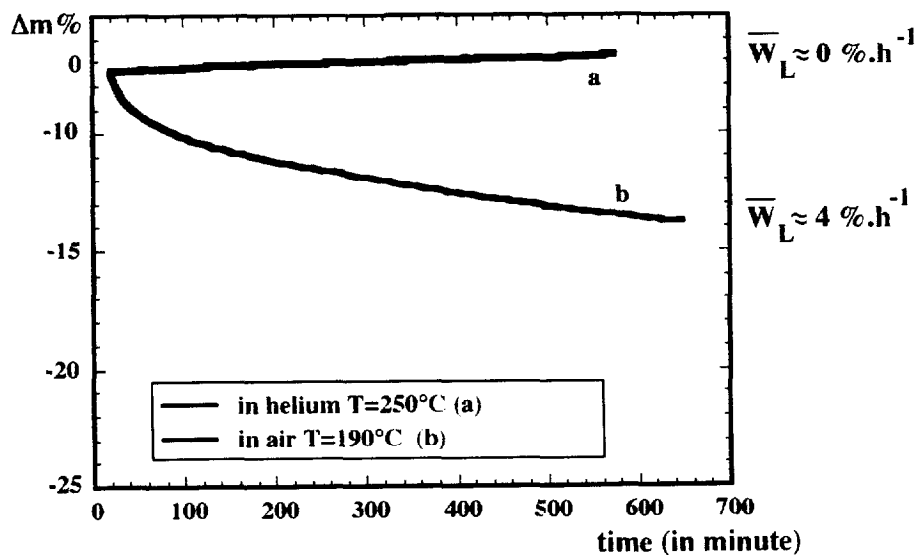


Fig. 2. Thermal stability for the electrolyte complex NPC1000/LiTFSI.

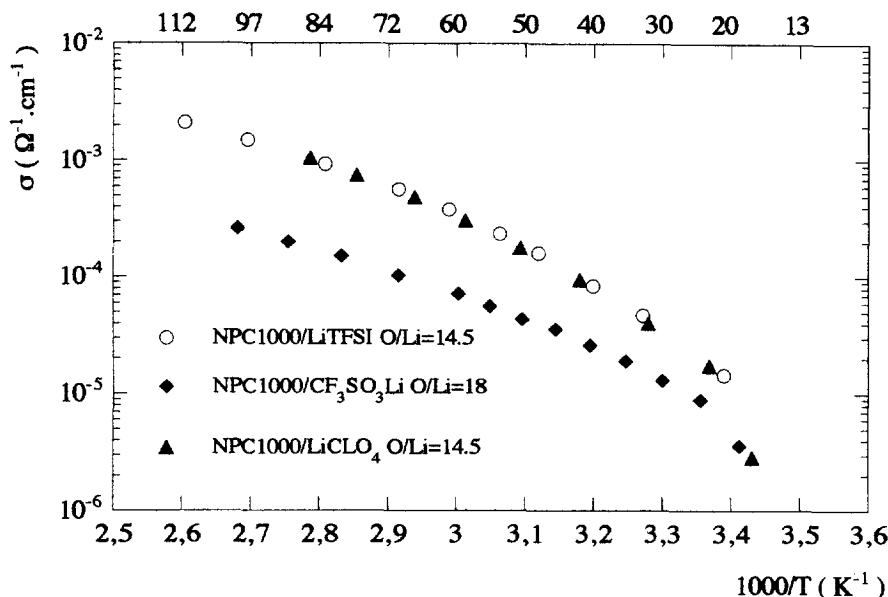


Fig. 3. Best conductivity values for several NPC1000/lithium salt electrolytes. NPC1000: network polycondensate 1000.

our network electrolytes, one may assume that in the case of the previous short-circuit, the overall volatile by-products released should be lower than 4%, thus providing the battery with a high safety level.

2.2.2. Mechanical stability

The thickness of the polymer electrolyte and the resistance of the electrolyte depend strongly on the mechanical properties of the polymer electrolytes. Young modulus ranging from between 0.5 and 1 MPa and elongation at break index close to 500% were measured at 60 °C on LiTFSI/NPC1000 electrolytes. Dynamic mechanical analyses have been performed and gives a storage modulus of 1 MPa on the rubbery plateau at a temperature higher than 30 °C [12]. A decrease in the cross-link density allows elongation to be reached at break index higher than 700%. It is therefore possible to adapt the material to the specifications of the battery manufacturer.

2.3. Ionic conductivities

We already reported an increase in conductivity of two orders of magnitude provided by substituting lithium triflate by lithium imide in polydioxolane-based polymer electrolytes [13]. But the same goes for an improvement of the host polymer, and surprisingly the amorphous cross-linked polycondensate matrixes, NPC1000, provide the same conductivity maxima with lithium perchlorate and lithium imide as shown in Fig. 3. These values obtained from cross-linked matrixes thoroughly washed, in order to remove any soluble polymer, are slightly lower than those obtained by using non-washed matrixes.

Comparison of the conductivity of polymer electrolytes based on EO/AGE networks shows that the highest conductivities are obtained by cross-linking anionic EO/AGE copolymers (Fig. 4).

Fig. 5 gives a comparison between cross-linked electrolytes prepared from the same copolymer. The only difference lies in the cross-link density as, the double bonds were partially hydrogenated. Despite a low impact on T_g , we must emphasize an enhancement in conductivity provided by decreasing the cross-link density.

2.4. Lithium salts

Due to the redox stability requirements (see design of the host polymer) most of the polar groups must be avoided, resulting in a low dielectric constant host polymer. Considering that the polyethers have a low AN, they show poor solubility towards the anions. These must therefore be selected from low nucleophilic anions with a well-delocalized negative charge. At the same time, they must be stable versus both metallic lithium and cathode material. These last years we investigated polymer electrolytes based on LiTFSI, $(CF_3SO_2)_2NLi$. This imide salt decreases the crystallinity [14], decreases the recrystallization rate and enhances the conductivity of POE [15], but also of poly(dioxolane) [16] and even of amorphous poly(oxypropylene) [17]. The same phenomenon is observed, when substituting LiTFSI by a disubstituted carbanion $(CF_3SO_2)_2CHLi$, TFSMLi [18], but this effect is more limited. As for the bulky trisubstituted salt $(CF_3SO_2)_3CLi$ first investigated by Dominey et al. [19] in liquid organic solvents, its behaviour is very close to that of LiTFSI [20]. Whatever the conductivity gains provided by these new bulky salts, they must also be evaluated with

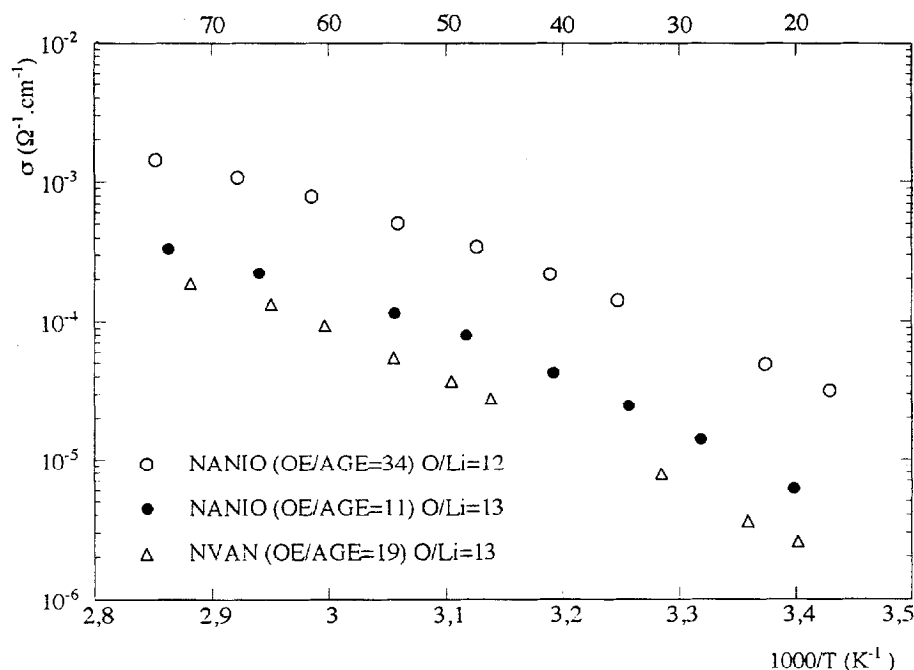


Fig. 4. Conductivity comparison between OE/AGE network/LiTFSI complexes. NANIO: network from anionic OE/AGE copolymer. NVAN: network from Vandenberg OE/AGE copolymer.

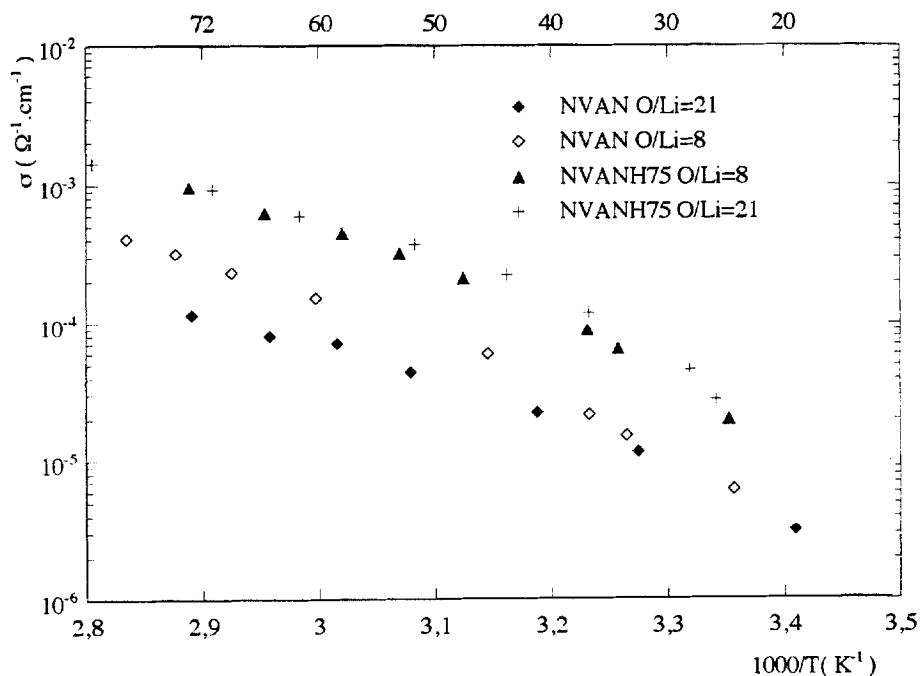


Fig. 5. Conductivity values of OE/AGE networks, according to the hydrogenation rate of AGE units. NVANH75: network from Vandenberg OE/AGE copolymer hydrogenated at 75%.

respect to their cationic transport numbers. In parallel with these salts, we pay special attention to salts in which a perfluorosulfonate anion is bonded to a polymeric backbone, comb copolymer or polyether network, to obtain single cation conductor polyethers.

In order to have a better understanding of the conduction mechanism, we investigated by ab initio calculations the optimized geometries and charge densities [21] on three anions CF_3SO_3^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ and $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$, and on the corresponding lithium-ion pairs. Though these calculations

are executed in gas phase, they may provide reliable information on the anions in condensed phase, as these suffer very weak interactions from the host polyethers. Although it was assumed that the CF_3SO_2 groups favour the negative charge delocalization, the *ab initio* calculations, in particular the NBO analysis, have to our knowledge for the first time established the existence and the extent of the anionic charge delocalization.

Moreover, the comparative conformational study (Fig. 6) of imide and carbanion shows that the transition barrier is by far lower in the imide (10 kJ/mol as compared with 40 kJ/mol) and might explain the imide 'plasticizing' behaviour, probably related to its bulkiness and flexibility. The conductivity maxima between LiTFSI/PEO and LiTFSM/PEO complexes are in a ratio 3 in favour of the former. We confirmed this result (non-published data) with NPC1000/LiTFSM complexes which are less conductive than both

LiClO₄ and LiTFSI complexes in NPC1000, the conductivity maxima is also in a ratio 3 in favour of LiClO₄ and LiTFSI complexes.

On the other hand NPA¹ atomic charges calculated on TFSM⁻ show a partial positive charge of the hydrogen atom equal to +0.304. We should stress that this partial positive charge increase in the lithium ion pair, as compared with TFSM⁻ reaches +0.326 in the lithium ion-pair [22]. This result is in agreement with the instability of the last hydrogen of the monoorganomagnesium salt of TFSM, $(\text{CF}_3\text{SO}_2)_2\text{CH}(\text{MgCl})$ which reacts with a second methylmagnesium chloride CH_3MgCl to give the resulting di-organomagnesium salt $(\text{CF}_3\text{SO}_2)_2\text{C}(\text{MgCl})_2$. From this result and from the partial positive charge, calculated by *ab initio*, a thermo-

¹ NPA: 'Natural population analysis' derived from 'natural bonding orbitals'.

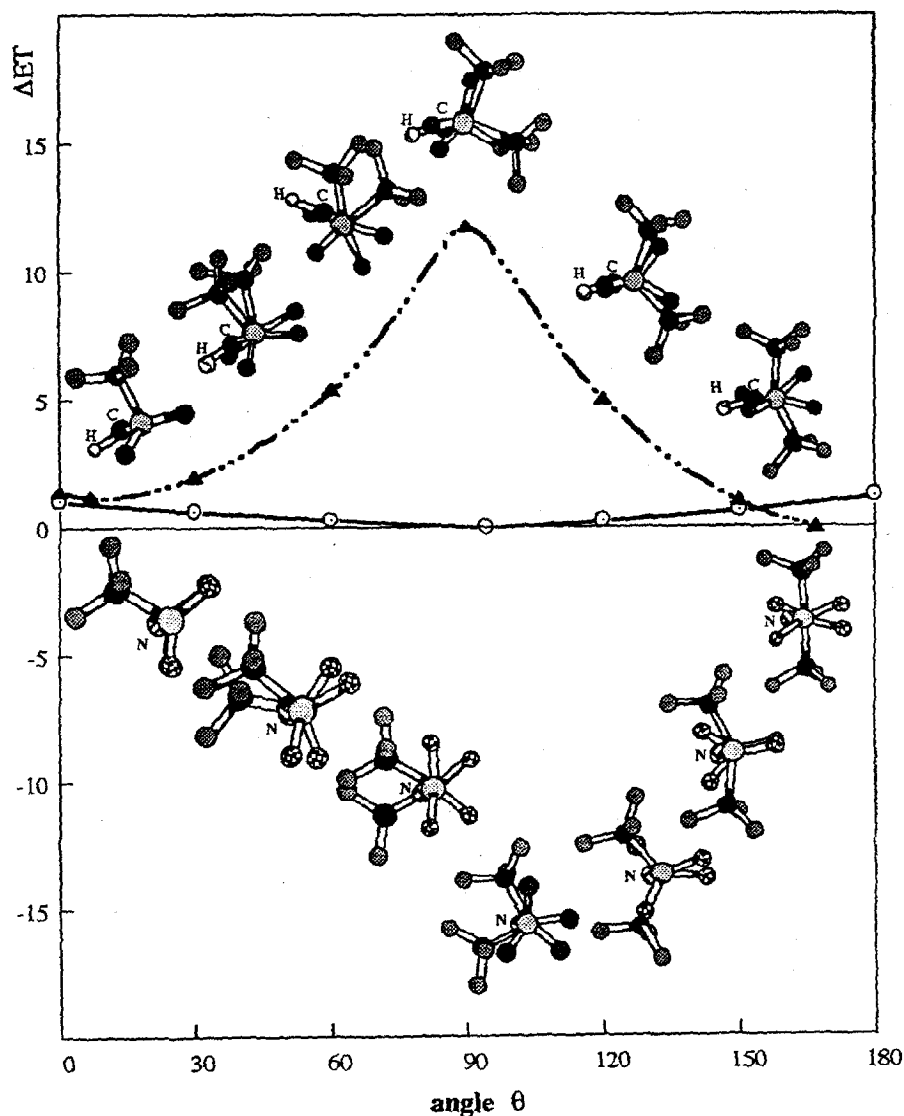


Fig. 6. Comparative conformational study of TFSI⁻ and TFSM⁻ anions.

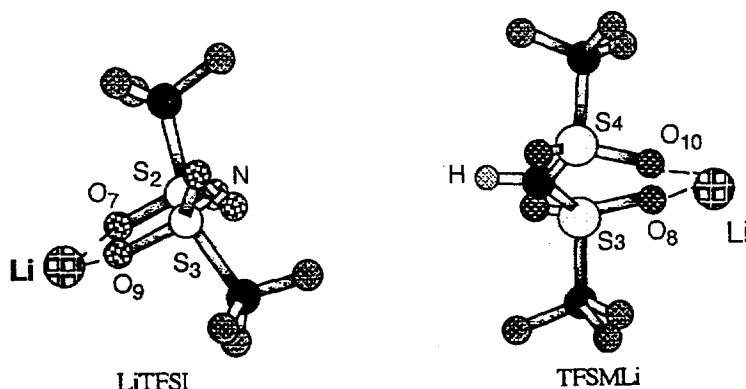


Fig. 7. More stable conformers of lithium-ion pairs.

dynamical instability of both TFSM^- and TFSMLi versus metallic lithium may be expected.

This theoretical result agrees well with our previous results on LiTFSM/POE complexes [18,20] which established the salt instability versus metallic lithium.

Cyclic voltammeteries, performed on micro- and macroelectrodes, show an instability in reduction which starts at about +0.2 V versus Li/Li^+ . This instability does not allow any lithium plating/stripping process; therefore, no oxidation peak, corresponding to $\text{Li} \rightarrow \text{Li}^+ + e^-$ reaction, is observed during the reverse scan. Moreover, the cyclic voltammogram is consistent with a hydrogen gaseous emission during the reduction process, and led us to assume that the methylene proton was of an acidic character. The wide electrochemical stability of the trisubstituted salt $(\text{CF}_3\text{SO}_2)_3\text{CLi}$, in which the methylene hydrogen has been substituted by a third electron-withdrawing group, supports this assumption.

The HOMO² value of the anions may also be related to their relative stability versus oxidation. From these values the stability decreases according to imide > triflate > carbanion. Finally, the study of the lithium-ion pairs shows that in both imide and carbanion salts the more stable conformers correspond to a Li^+ 'chelated' between two oxygen atoms each belonging to a different SO_2 group (Fig. 7).

3. Conclusions

Several polymer electrolytes meet the requirements of redox stability and high conductivity. The selection of simple reactions allows the polymerizations and polycondensations to be scaled-up. The thermal and mechanical stabilities of polymer electrolytes offer safety warranties and enable the film thickness to be decreased, thus lowering the electrolyte resistance. Finally, the use of dry polymer electrolytes is not restricted to lithium batteries consisting of a metallic lithium anode and may be extended to any type of negative electrode.

² HOMO value: highest occupied molecular orbital.

Acknowledgements

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