

Comparative ion transport in several polymer electrolytes

F. Alloin ^{*}, D. Benrabah, J.-Y. Sanchez

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

Accepted 25 November 1996

Abstract

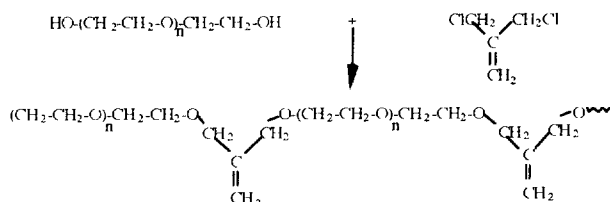
A comparative transport number study on a wide variety of lithium salts was performed, confirming the prevalence of an anionic transport in most of the usual salts dissolved in a polyether network. A cationic transport close to 0.5 was determined for several perfluorosulfonate-based polymer electrolytes. The method used confirmed a transport number close to unity for a perfluorosulfonate-based ionomer. © 1997 Elsevier Science S.A.

Keywords: Polymer electrolytes; Transport number; Poly(oxyethylene) network; Lithium salts; Ionomers

1. Introduction

Contrary to glass or ceramic electrolytes and except for ionomers, both cations and anions contribute towards the conductivity of polymer electrolytes. Therefore, in addition to the determination of their ionic conductivities and electrochemical stability range, a good method to compare the performance of polymer electrolytes consists in measuring the transport numbers and diffusion coefficients. Functional groups, i.e. polar protic groups, which induce anionic solvation through hydrogen bonds, may modify the mobility of anions, cations, or both anions and cations. Protic and some aprotic groups react in presence of lithium, while others are unstable versus most of the cathode materials. The polymer matrix must be therefore accurately selected. In this contribution we will compare the lithium transport number for several salts dissolved in high molecular weight linear poly(oxyethylene) (POE) and cross-linked polyethers NPC (network poly(isobutenyloligooxyethylene)).

The cross-linked polyethers were obtained by a step-growth polymerization between poly(ethylene glycol) 1000 and a dihalide unsaturated compound 3-chloro-2-chloromethyl-1-propene [1]. The Williamson-type polycondensation proceeds [2], according to the following scheme, in NaOH or KOH solutions



Due to the incorporation of the isobutenyl moiety, the resulting polyethers show a clear decrease in crystallinity and melting point as compared with the linear POE and even to the starting poly(ethylene glycol). The isobutenyl groups allow further free-radical cross-linking, again decreasing crystallinity and melting point when compared with the linear polycondensate. Finally, the isobutenyl moiety may copolymerize with a monomer bearing an ionophoretic function, resulting in a single cation conductor polyether network.

We compared t_{Li^+} , at several concentrations, for Li-TFSI, $(CF_3SO_2)_2NLi$, $LiClO_4$, CF_3SO_3Li , $TriTFSMLi$, $(CF_3SO_2)_3CLi$, as well as for non-bonded unsaturated salts such as a diallyl amide by-product $DaaR_fSO_3Li$, $(CH_2=CH-CH_2)_2NCO-CF(CF_3)SO_3Li$, and an allyloxy by-product AlR_fSO_3Li , $CH_2=CH-CH_2-O-CF_2-CF_2SO_3Li$ [3].

2. Experimental

2.1. Polycondensation reaction

The linear unsaturated polycondensates were prepared in bulk, according to the typical procedure already described for

^{*} Corresponding author.

α,ω -dihydroxyoligo(oxyethylene) [1]. PEG1000 (from Aldrich) and 3-chloro-2-chloromethyl-1-propene were used in a molar stoichiometric ratio. The average mol. wt. \bar{M}_w and \bar{M}_n were determined in tetrahydrofuran (THF) by GPC, Waters 590 and a data module Waters 745B, and expressed in a polystyrene equivalent. We found $\bar{M}_w = 105000$, $\bar{M}_n = 47000$ and $I = \bar{M}_w / \bar{M}_n = 2.2$.

2.2. Cross-linking of the membrane

The films were prepared by free-radical polymerization at 70 °C, using benzoyl peroxide as an initiator. The resulting membranes were washed several times in methanol, and dried under vacuum. The electrolyte films were obtained by swelling the films in an acetonitrile preweighted salt solution.

In order to obtain a single-cation conductor, DaaR_pSO₃Li salt has been attached, by covalent bonding, to the unsaturated polyether by free-radical copolymerization of the salt and the polyether double bonds. The polycondensate cross-linking is therefore achieved, simultaneously with the salt grafting. In order to avoid any contamination by non-grafted salt, the membranes were thoroughly washed in methanol to eliminate residual free salt.

2.3. Thermal analysis

Glass transition temperature (T_g) and melting temperature were measured in helium using a Netzsch STA409 thermal analyser. In the typical protocol, samples are first cooled from room temperature to -120 °C, then heated again at 10 °C min⁻¹ to 150 °C. After this first heating cycle the samples are quenched to -120 °C and then heated at a rate of 10 °C min⁻¹.

2.4. Ionic conductivity

The ionic conductivities of various complexes were obtained by impedance spectroscopy using stainless-steel

blocking electrodes and an HP4192A impedance analyser over the frequency range 5 Hz to 13 MHz.

2.5. Electrochemical study

The transport number t_{Li^+} determination in polymer electrolytes was performed, by means of a combination of complex impedance measurements and potentiostatic polarization measurements, sandwiching the samples between two metallic lithium electrodes [2]. The amplitude of the impedance measurements and the polarization voltage were kept at 10 mV. Polarization measurements were carried out with a Mac Pile computer device, allowing 0.25 μ A and 1.25 mV accuracy on intensity and voltage, respectively.

3. Results and discussion

3.1. Ionic conductivity

The ionic conductivities of NPC1000-based cross-linked electrolytes with several salts were investigated. Fig. 1 presents the best conductivities obtained with these different salts. The best were obtained with LiTFSI and LiClO₄ reaching 2×10^{-5} S cm⁻¹ at room temperature and 10^{-3} S cm⁻¹ near 80 °C. As for CF₃SO₃Li, TriTFSMLi and DaaR_pSO₃Li showed ambient temperature conductivities (25 °C) close to 7×10^{-6} S cm⁻¹. At higher temperature, 80 °C, TriTFSMLi appeared more conductive than CF₃SO₃Li and DaaR_pSO₃Li reaching 3×10^{-4} S cm⁻¹ but remained markedly less conductive than LiTFSI complexes (factor 5). Although the conductivity study of TriTFSMLi complexes was performed in a somewhat limited salt concentration range $6 < O/Li < 33$, this result was surprising and not in agreement with a previous study performed on linear POE: 5×10^6 [3] which established that LiTFSI-POE and TriTFSMLi-POE complexes reached about the same conductivity maxima. Regarding the single-cation conductor NPC1000/DaaR_pSO₃Li, its Arrhe-

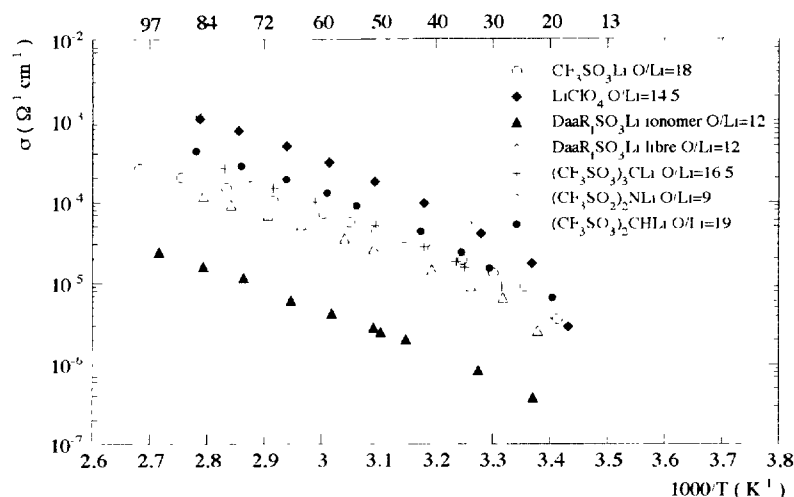


Fig. 1. Comparison of best conductivity levels for several NPC1000/lithium salt complexes

nus plot showed a conductivity value close to $4 \times 10^{-7} \text{ S cm}^{-1}$ at 25°C , so one order of magnitude smaller than that observed with the same concentration of non-attached salt, dissolved in NPC1000 network.

The Arrhenius plots of NPC1000-based polymer electrolytes exhibit free volume behaviour, above room temperature (25°C). This behaviour is in agreement with the differential scanning calorimetry (DSC) recording which shows that all the lithium salts complexes are, independently of their concentration, completely amorphous above 25°C . T_g of Tri-TFSMLi complexes are very close to those of LiTFSI with, for instance, $T_g = -44.2^\circ\text{C}$ for the former, as compared with -43.5°C obtained for NPC1000/LiTFSI at the same salt concentration ($\text{O/Li} = 15$). Single-ion conductor electrolytes (NPC1000/DaaR₁SO₃Li) exhibited very low T_g ($T_g = -67.6^\circ\text{C}$). This phenomenon has often been observed with cross-linked ionomers [4,5].

3.2. Li^+ transport number

It has been noted [6,7] that this method over-estimates a cationic transport number in the situation where aggregates or ionic associations exist in the electrolyte. The ionic association occurs in such low polarity media in accordance with spectroscopy studies [8,9].

Most of the experiments were carried out at 80°C . Transport number measurements were performed on LiTFSI-based polymer electrolytes, using two host polymers, namely linear poly(oxyethylene) POE = $5 \times 10^6 \text{ g mol}^{-1}$ and the cross-linked polycondensate, NPC1000. These electrolytes exhibited the same behaviour with a cationic transport number close to 0.1 (Fig. 2), these values were close to those determined by Watanabe and Nishimoto [10] in different polyether networks. A slight increase in cationic transport number is observed when decreasing the salt concentration.

As observed, architectural modifications, with respect to linear crystalline POE, do not induce a modification in LiTFSI

transport numbers when the salt is dissolved in an NPC1000 host polymer. As the single-ion conductor is prepared from NPC1000, we selected therefore to perform the transport number comparison in the NPC1000 host polymer rather than in POE.

Cationic transport number t_{Li^+} evolutions with salt concentrations are given at the same temperature (80°C) for different lithium salts, in Fig. 3. The lowest t_{Li^+} was obtained with LiTFSI, while t_{Li^+} is about twice as high in the methide salt, TriTFSMLi, but remained very low. As for LiClO₄, we found $t_{\text{Li}^+} \sim 0.2$, which was higher than that, 0.11, reported by Watanabe and Nishimoto [10]. The best results were obtained with the perfluorosulfonate salts, both unsaturated salts DaaR₁SO₃Li and AlR₁SO₃Li exhibiting t_{Li^+} values higher than those determined for LiCF₃SO₃. We must emphasize the $t_{\text{Li}^+} = 0.6$ value obtained for DaaR₁SO₃Li, but also the values close to 0.5 obtained with the other perfluorosulfonate salts. t_{Li^+} values are slightly sensitive to the polymer electrolyte composition, t_{Li^+} decreasing generally at high concentration. If DaaR₁SO₃Li provides the highest t_{Li^+} values when the salt is only dissolved in NPC1000, it allows us to reach a cationic transport number close to unity when attached to the macromolecular backbone. Indeed the experimental values, ranging between 0.92 and 0.96, are in full agreement with the theoretical values and support the effectiveness of this electrochemical method.

Table 1 reports the lithium conductivities, $\sigma^+ = \sigma t_{\text{Li}^+}$, for the different salts. The highest cationic conductivity, $2 \times 10^{-4} \text{ S cm}^{-1}$ at 80°C , was obtained for NPC1000/LiClO₄ complex. Surprisingly, the cationic conductivities of LiTFSI, non-bonded DaaR₁SO₃Li and CF₃SO₃Li are very close at 80°C . From this comparison we may be optimistic about the potentiality of DaaR₁SO₃Li, since the electrolyte composition has not been optimized.

Nernst–Einstein relationship $D_i = \sigma_i RT / F^2 C_i$ allows the diffusion coefficient to be calculated, at 80°C , for the different ions (Table 2). Obviously NPC1000/LiClO₄ electrolyte

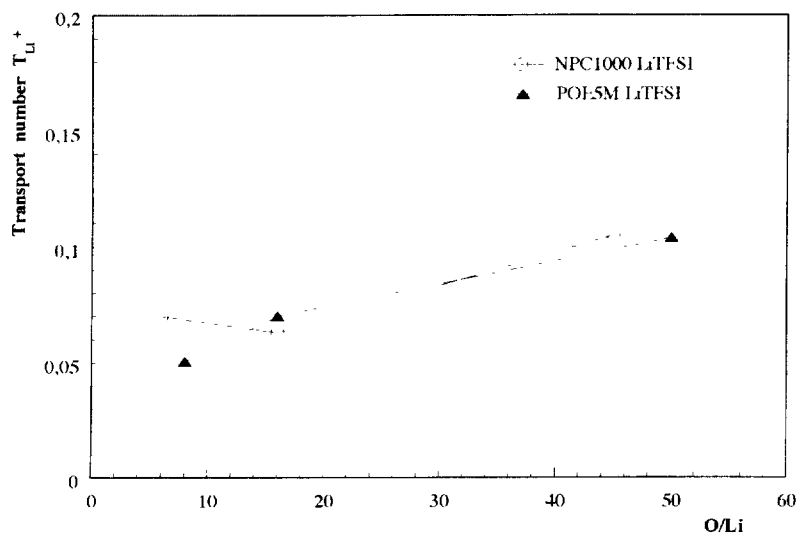


Fig. 2. Comparison of lithium transport number in LiTFSI salt using two different host polymers

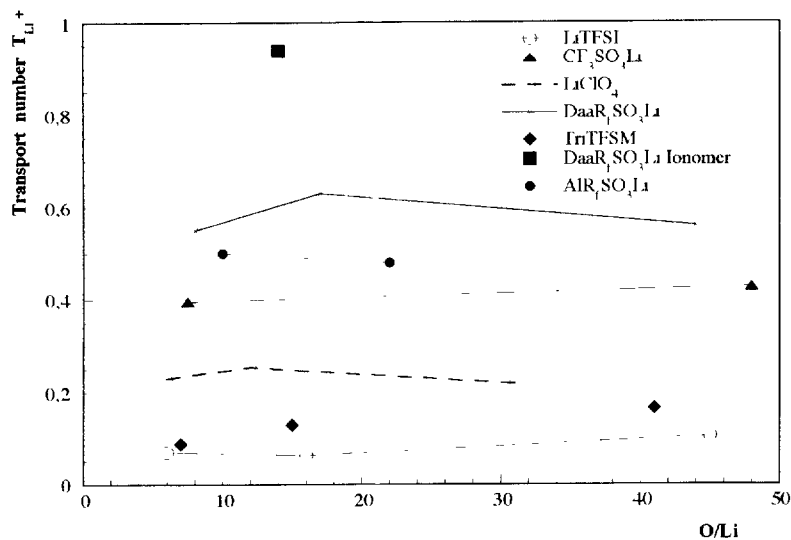


Fig. 3. Lithium transport number in several NPC1000/salt complexes.

Table 1
Cationic conductivity values for several salts at 80 °C

	σ^+ ($\Omega^{-1} \text{cm}^{-1}$)
LiTFSI O/Li = 14	4.85×10^{-5}
CF ₃ SO ₃ Li O/Li = 18	6×10^{-5}
LiClO ₄ O/Li = 14	1.8×10^{-4}
TriTFSM O/Li = 15	3.24×10^{-5}
DaaR ₇ SO ₃ Li O/Li = 12	5.7×10^{-5}
DaaR ₇ SO ₃ Li ionomer O/Li = 12	1.3×10^{-5}

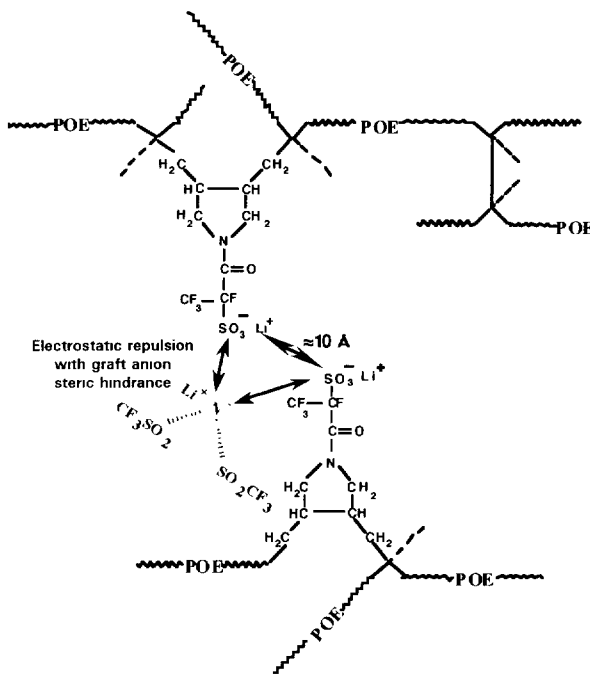
Table 2
Anionic and cationic diffusion coefficients for complexes NPC1000/lithium salt

	D_{lithium} ($\text{cm}^2 \text{s}^{-1}$)	D_{anion} ($\text{cm}^2 \text{s}^{-1}$)
LiTFSI O/Li = 14	1.32×10^{-8}	2.1×10^{-7}
CF ₃ SO ₃ Li O/Li = 18	9.76×10^{-9}	2.9×10^{-8}
LiClO ₄ O/Li = 14	4.9×10^{-9}	1.5×10^{-7}
TriTFSMLi O/Li = 15	7.6×10^{-9}	5.6×10^{-8}
DaaR ₇ SO ₃ Li O/Li = 12	1.23×10^{-8}	1.45×10^{-8}
DaaR ₇ SO ₃ Li ionomer O/Li = 12	3×10^{-9}	

exhibits the highest lithium coefficient with $4 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$ at 80 °C, this in contrast to NPC1000/LiTFSI electrolytes presenting the highest anionic mobility with an anion diffusion coefficient of $2 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$.

In single-cation cross-linked networks the anion mobility is restricted to the segmental fluctuations around its equilibrium position. We may therefore assume that the grafted anions behave as 'immobile pillars', a rapid calculation, taking into account the specific mass of the electrolyte, showing that the average distance between two grafted anions should be close to 6 Å for O/Li = 12 and should not exceed 10 Å for O/Li = 60. In case of a mixture of free-salt and single-cation conductor we might assume that, due to steric hindrance, the 'immobile pillars' should not favour the TFSI⁻ anion mobility. Indeed, recent ab initio calculations performed on the

TFSI anion, allow us to determine, from the optimized geometries, a minimum bulkiness between 6 and 9 Å. In addition, local electrostatic repulsions should take place between the free-anions and the 'immobile pillars', as exhibited below



Both steric hindrance and electrostatic repulsions should therefore notably decrease the free-anions mobility. To check the validity of our assumption, we performed a measurement on a cross-linked single-cation network NPC1000/DaaR₇SO₃Li⁻Li⁺, in which LiTFSI was incorporated. The membrane NPC1000/DaaR₇SO₃Li, previously washed in methanol to remove non-bonded DaaR₇SO₃Li, has been dried and weighted, before swelling in acetonitrile solution of LiTFSI. After the removal of acetonitrile the membrane has been weighted, the weight difference allowing the TFSI/Li composition to be calculated. Table 3 gives the cationic

Table 3
Transport numbers for mixed 'free'/'grafted' lithium salts

	t^+
DaaR ₇ SO ₃ Li O/Li = 12 + LiTFSI O/Li = 8	0.119
DaaR ₇ SO ₃ Li O/Li = 12 + LiTFSI O/Li = 12	0.12
DaaR ₇ SO ₃ Li O/Li = 25 + LiTFSI O/Li = 17	0.113

transport numbers determined for both salts. Unfortunately, although t_{Li^+} values increase from 50 to 100%, they still remain very low and close to 0.1. Anionic diffusion, contrary to our assumption, has not been decreased by the presence of the 'immobile pillars'.

4. Conclusions

This preliminary study allowed an ion transport comparison to be performed in a wide variety of lithium salts, using a poly(oxyethylene) network as the host polymer. A prevalent anionic transport has been found for most of the lithium salts, notably for LiTFSI and LiTriTFSM. On the contrary, perfluorosulfonate-based salts exhibited t_{Li^+} values close to 0.5, and the high t_{Li^+} value, close to 0.6, calculated for the

DaaR₇SO₃Li complexes. On the other hand, t_{Li^+} close to unity, has been found for DaaR₇SO₃Li grafted in the NPC1000 network, confirming the single-ion conductivity of these membranes. Other transport number methods are at present in progress to check these values.

References

- [1] F Alloin, J.-Y. Sanchez and M. Armand, *J. Electrochem. Soc.*, **141** (1994) 1915.
- [2] J. Evans, C.A. Vincent and P.G. Bruce, *Polymer*, **28** (1987) 2324.
- [3] D. Benrabah, D. Baril, J.-Y. Sanchez, M. Armand and G. Gard, *J. Chem. Soc. Faraday Trans.*, **89** (1993) 355.
- [4] D. Benrabah, S. Sylla, F. Alloin, J.-Y. Sanchez and M. Armand, *Electrochim. Acta*, **40** (1995) 2259.
- [5] D. Benrabah, S. Sylla, J.-Y. Sanchez and M. Armand, *J. Power Sources*, **54** (1995) 456.
- [6] P.G. Bruce and C.A. Vincent, *Faraday Discuss. Chem. Soc.*, **8** (1989) 43.
- [7] G.G. Cameron, J.-L. Harvie and M.D. Ingram, *Solid State Ionics*, **34** (1989) 65.
- [8] G. Petersen, L.M. Torell, S. Panero, B. Scrosati, C.J. Da Silva and M. Smith, *Solid State Ionics*, **60** (1993) 55.
- [9] M. Kakihana, S. Schantz, L.M. Torell and J.R. Stevens, *Solid State Ionics*, **40/41** (1990) 641.
- [10] M. Watanabe and A. Nishimoto, *Solid State Ionics*, **79** (1995) 306.