

ARTICLES

NMR Study of Cation, Anion, and Solvent Mobilities in Macroporous Poly(vinylidene fluoride)

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Received: March 23, 2004; In Final Form: September 10, 2004

The mobilities of lithium, PF_6^- and solvents in the electrolyte LiPF_6 —(ethylene carbonate—dimethyl carbonate—diethyl carbonate) were measured using the pulsed gradient spin—echo NMR. They were compared to those of the same electrolyte filling a macroporous poly(vinylidene fluoride) membrane. The conductivity decrease resulting in the incorporation of this macroporous membrane and the cationic transport number were analyzed in terms of (i) solvent/polymer and solvent/salt interactions, (ii) ionic dissociation, and (iii) tortuosity.

Introduction

To obtain thin and flexible batteries adapted to the evolution of portable electronics, the old concept¹ of gelled polymer electrolyte has recently been studied using several thermoplastic or cross-linked polymer matrixes such as polyacrylonitrile (PAN),^{2–4} poly(methyl methacrylate) (PMMA),^{5,6} polymethacrylonitrile (PMAN) networks,⁷ or poly(vinylidene fluoride)—hexafluoropropene (PVdF—HFP).^{8,9} Generally, prior to the battery formation, the gelled polymer electrolyte is prepared by swelling the polymer matrix with the liquid electrolyte. Lithium-ion battery manufacturers, however, prefer a “dry” approach consisting of assembling a PVdF membrane free of electrolyte with the electrodes. The electrolyte is added just before the first charge of the battery. As the battery is stored free of electrolyte, (i) the moisture contamination is very low and (ii) self-discharge does not occur. These sets, i.e., membrane + liquid electrolyte, must not be considered gels but multiphase systems, where both porous structures, filled by the electrolyte and polymer gelled by the electrolyte, coexist. The use of polymer electrolyte based on a macroporous PVdF¹⁰ separator would simplify the cell design. [The word microporous has been used for a very long time to refer to porous polymeric membranes, even when the average porous diameter is close to 0.5 μm . According to IUPAC rules it is recommended to refer to them as macroporous membranes.] Indeed, the use of a sealed packaging, to prevent solution leakage, is not required as this separator has enough affinity with the usual electrolyte solvents. The macroporous membrane may be considered to some extent as a composite material, consisting of an electrolyte solution and of an interpose semicrystalline polymeric matrix. The conductivity, mainly dominated by the solution, is related to

(i) the separator porosity, (ii) its tortuosity, and (iii) its wetting by the liquid electrolyte. However, due to its polar nature, PVdF matrix interacts with the carbonate solvents and this influences the conductivity of the set PVdF + liquid electrolyte. To show the consequences of the polymer/solvent interactions on the battery performances, several studies^{11–13} were performed on swelling ability, swelling selectivity, and physical transformation of a PVdF macroporous membrane in the presence of an electrolyte.

In previous papers pulsed field gradient spin—echo (PFG spin—echo) nuclear magnetic resonance, NMR, measurements of the self-diffusion coefficients of solvents, lithium, and anions were performed, both in liquid electrolytes¹⁴ and PVdF gelled electrolytes.^{15–18}

We investigated the effect induced by the use of a PVdF macroporous separator on the conductivity in order to find, between tortuosity and polymer/solvent interactions, the prevalent factor on the conduction performance. The present paper describes PFG spin—echo NMR measurements performed on macroporous PVdF incorporating ethylene carbonate—dimethyl carbonate—diethyl carbonate, EC—DMC—DEC (2–2–1) LiPF_6 (1 M) as a liquid electrolyte.

Experimental Details

Preparation of the PVdF Macroporous Membrane. A 100 μm thick macroporous PVdF membrane was prepared as follows: 3.4 g of PVdF (301F Atofina) was dissolved in 16.6 g of dimethyl ketone at 60 °C in a hermetically closed vessel. The solution was then cast in a thickness of approximately 500 μm on an aluminum support, put into a bath made of pure ethanol for 45 s, and dried, first at room temperature and then at 60 °C overnight.

Preparation of the Dense PVdF. The dense PVdF membranes were obtained by hot-pressing PVdF powder (205 °C) via the fast tempering of polymer films. It was the only way to obtain easily, and in a reproducible way, true dense membranes.

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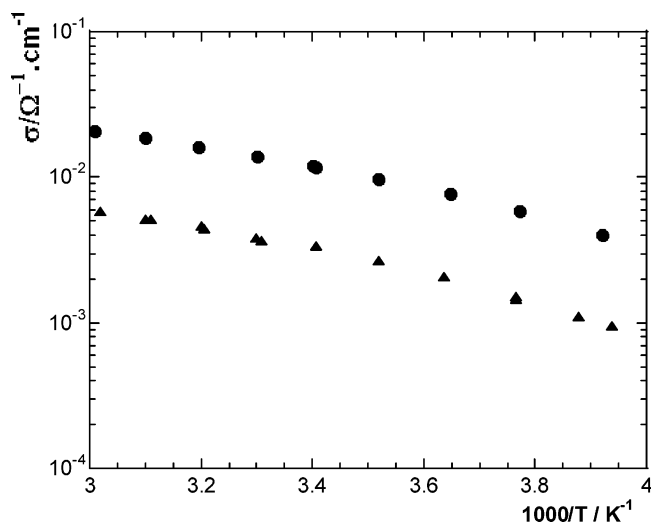


Figure 1. Conductivity comparison of (●) liquid electrolyte EC/DMC/DEC (2/2/1) + 1 M LiPF₆ and (▲) macroporous membrane with EC/DMC/DEC (2/2/1) + 1 M LiPF₆.

Liquid Electrolyte. The “battery grade” solvents EC, DMC, and DEC (<30 ppm H₂O) from Merck were further dried over an activated molecular sieve (3 Å) before use (<5 ppm H₂O). The LiPF₆ battery grade, manufactured by Merck was used as received.

Pulsed Gradient Spin–Echo NMR. The experiments were performed by means of a homemade spectrometer at the Larmor frequency in the interval 30–300 MHz and a superconducting coil to give a direct magnetic field of 6.6 T. Details of the diffusion coefficient measurements are given elsewhere.¹⁹ The usual pulsed magnetic gradient technique and a sequence described by Stejskal and Tanner were used.²⁰ The magnetic field gradient pulses were delivered by a Techtron power supply; the maximum constant current reached 60 A during a period of 5 ms. The amplitude of the magnetic field gradient was varied between 0 and 900 G/cm, and the time interval between the two magnetic field gradient pulses was varied between 30 and 100 ms. Their duration was fixed at 3 ms. This allowed us to observe the attenuation of a spin–echo amplitude over a range of about 30, providing good accuracy (5%) of the values determined for the self-diffusion constants. The time dependence of the transverse nuclear magnetization, $g(t)$, of the proton nuclei (¹H) were performed by the usual Han spin–echo technique with a $(\pi/2 - \tau - \pi)$ sequence. All $g(t)$ were normalized to one, i.e., $g(0) = 1$.

Ionic Conductivity Measurements. The conductivity of the liquid electrolytes was measured using a Tacussel cell with a geometrical factor near 1 cm^{−1}. Conductivity measurements of the dense or macroporous membranes of PVdF were carried out in button type coin cells (CR 2430) with stainless steel electrode of small diameter to increase the measuring accuracy. All measurements were carried out under argon by impedance spectroscopy over the frequency range of 5–13 MHz, using an HP 4192A analyzer.

Results and Discussion

Liquid Electrolyte. Conductivity. The liquid electrolyte is a solution of LiPF₆ in a mixture of solvents (EC/DMC/DEC) whose volumetric composition 2/2/1 provides good conductivities in all the temperature range between −20 °C and +60 °C (Figure 1). The salt concentration used (1 mol/L) is close to that corresponding to the conductivity optimum. The presence of EC provides a high permittivity and induces a high dissocia-

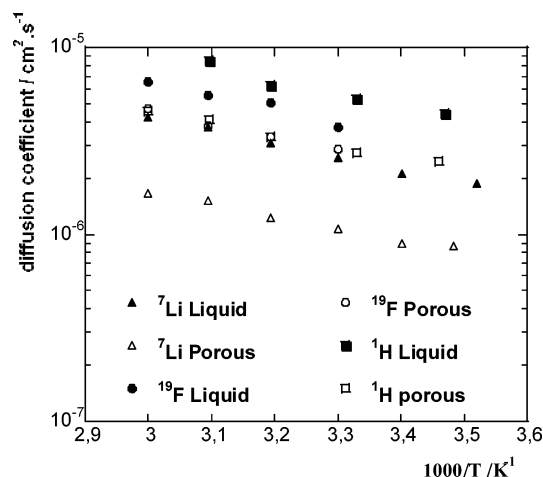


Figure 2. Self-diffusion coefficients of lithium, anion, and proton species in macroporous polymer electrolyte and in liquid electrolyte.

tion, resulting in a high concentration in free ions. The use, as a third solvent, of DEC (i) improves the electrolyte performances at low temperature, with respect to binary EC/DMC (1/1) solvent mixtures and (ii) prevents the electrolyte recrystallization down to −20 °C.

Pulsed Gradient Spin–Echo NMR. Figure 2 shows the diffusion coefficients, vs temperature, of lithium and anion through the nucleus ⁷Li, ¹⁹F. First of all, it must be pointed out that the diffusion coefficients for the solvent molecules are slightly higher than that of PF₆[−], while the lithium ones are notably lower. These results are in agreement with the conclusions of Hayamizu et al.¹⁴ who measured lithium trifluoromethanesulfonylimide, LiTFSI, diffusion coefficients in various organic electrolytes. They reported a linear relationship between the ion and solvent diffusions, which indicates that the ion diffusion is governed by the diffusion of the solvent and that the Stokes–Einstein equation

$$D = kT/(6\pi\eta r_s)$$

is valid, in which η is the solvent viscosity, D is the self-diffusion coefficient, r_s is the effective hydrodynamic radius, T is the temperature, and k is the Boltzmann constant.

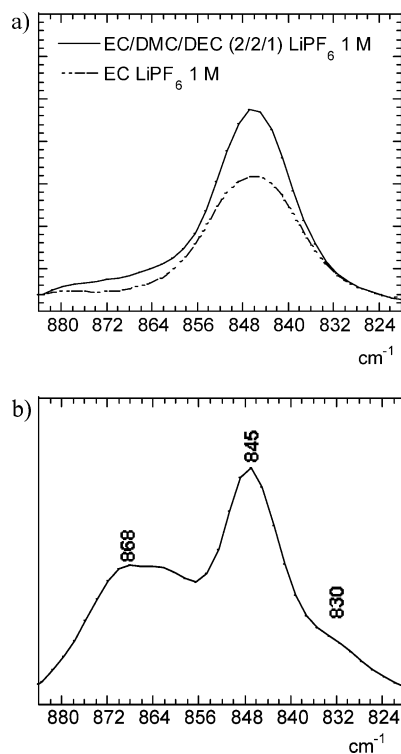
It must be remembered that aprotic solvents such as cyclic or acyclic carbonates have fairly low acceptor number values (AN), leading therefore to a poor solvation ability vs anions. The ratio of the diffusion coefficients should, therefore, be proportional to the reverse of the radius ratio of the species. The radii of PF₆[−] (0.254 nm) and Li⁺ (0.076 nm) were calculated by the MM² method;²¹ the PF₆[−] radius is very close to that of a cyclic carbonate as PC (0.276 nm), which might explain the low difference between anion and solvent diffusion coefficients. On the other hand, the gap between the diffusion coefficients of lithium and solvents may be related to the cation solvation. This solvation strongly increases the effective hydrodynamic radius of the diffusing species.

The lithium transference numbers t^+ , calculated from the diffusion coefficient, using $t^+ = D(\text{Li}^+)/[D(\text{Li}^+) + D(\text{PF}_6^-)]$, are equal to 0.4, independently of the temperature. This value is in good agreement with those obtained by Hayamizu et al.¹⁴ in carbonate solvents.

Since the self-diffusion coefficient is related to all the species, i.e., isolated, ion-pair, and solvated states, these experimental values are in fact average values. However for free ions and solvent-separated ion pairs, the Nernst–Einstein equation may be used to calculate the ionic conductivity, σ_{calc} , from the

TABLE 1: Measured and Calculated Conductivities of the Liquid Electrolyte EC/DMC/DEC (2/2/1) + LiPF₆ (1 M)

T (°C)	σ_{calc} (S·cm ⁻¹)	σ_{exp} (S·cm ⁻¹)	$\sigma_{\text{exp}}/\sigma_{\text{calc}} = \xi^a$
30	2.3e^{-2}	1.4e^{-2}	0.62
60	3.63e^{-2}	2.1e^{-2}	0.6

^a ξ : dissociation degree.**Figure 3.** IR spectra of the $\nu_3(\text{PF}_6^-)$ of the PF_6^- anion for (a) in EC/LiPF₆ (1 M) and in EC/DMC/DEC (2/2/1) + 1 M LiPF₆ and (b) DMC/LiPF₆.

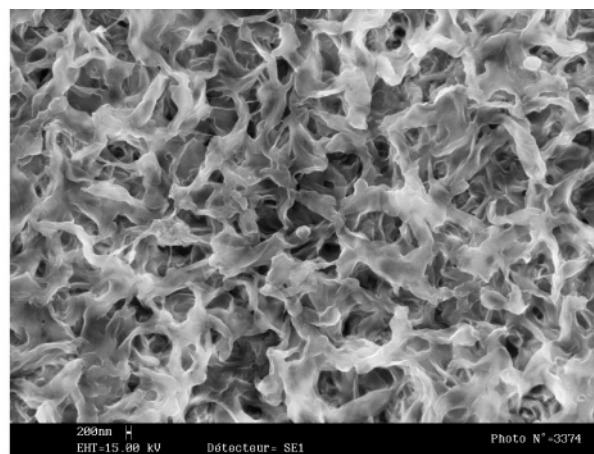
diffusion coefficient of the cation $D(\text{Li}^+)$ and anion $D(\text{PF}_6^-)$ as

$$\sigma_{\text{calc}} = Nq^2/kT[D(\text{Li}^+) + D(\text{PF}_6^-)]$$

where q is the charge on each ion and N is the number of anions and cations per volume unit. The Nernst–Einstein equation only allows the order of magnitude of the dissociation ratio to be determined. Indeed, this relation is valid for the infinitely dilute state, far from the salt concentration in electrolytes. However, it has been reported that calculated dissociation degrees were in good agreement with, for example, IR investigations.^{19,22}

Generally, due to ionic associations, as contact ion pair and aggregates which behave as neutral species, calculation from NMR diffusion coefficients generally overestimates the conductivity values with respect to the experimental ones (σ_{exp}). The values of σ_{calc} and σ_{exp} are gathered in Table 1. The values σ_{calc} are higher, by a factor 1.7, than the experimental ones. This discrepancy might be related to a partial dissociation of the salt, leading to a dissociation degree close to 0.6, in good accordance with those reported¹⁴ in electrolytes based on cyclic carbonates, such as PC.

Infrared Spectroscopy Study. To check the previous assumptions about (i) the influence of the solvation on the lithium mobility and (ii) the salt partial dissociation, an infrared spectroscopy study was carried out on LiPF₆ solutions in various usual solvents EC, DEC, and DMC of liquid electrolytes.²³ These solvation numbers depend on the salt concentration and

**Figure 4.** SEM of macroporous PVdF surface.

on the solvent, but the values obtained range between 2 and 3, in agreement with reported values.²⁴

Attributions of the IR bands of the anion for compounds such as XPF₆ were previously reported.^{25–27} For PF₆⁻, the group theory indicates the existence of two bands allowed in IR. However inactive bands become slightly active because of the distortion of the octahedral symmetry of PF₆⁻ and the combination of the two bands allowed. By referring to other papers on LiAsF₆,^{24,28} it is possible by following up on the spectral bands of PF₆⁻ to detect the presence of free ions, ion pairs, or aggregates. For solvent having a quite high permittivity like dimethyl ketone LiAsF₆ spectra present essentially a great mean band at 700 cm⁻¹ that is associated with free ions. For solvents such as DMC, other bands are clearly visible: one at 676 cm⁻¹ characteristic of contact species and one at 717 cm⁻¹ characteristic of ion pairing.^{24,28} LiPF₆ salt dilutes at low concentration in EC, a solvent of great permittivity; we founded only one main great band at 845 cm⁻¹. As a consequence, by analogy with LiAsF₆ study, we have associated this salt band with free species. As the salt concentration is increased, we observe the growth of adjacent bands at 852 and 838 cm⁻¹ (Figure 3a). For solvents with low permittivity like DEC and DMC, the 845 cm⁻¹ band is no more the main band of the spectra, and we observe other great bands around 832 and 866 cm⁻¹ (Figure 3b). We associated these new bands between 852 and 866 cm⁻¹ and between 832 and 838 cm⁻¹ with ion pairs or aggregates, because they are clearly visible with low-permittivity solvent that cannot dissociate well the salt. Moreover their intensity grows with salt concentration as compared to that at 845 cm⁻¹.

One might therefore, in a first indexing, associate the band at 845 cm⁻¹ with free ions and the band at 866 cm⁻¹ with ion pairs or aggregates. The IR spectrum, associated with our ternary electrolyte LiPF₆ (1 M) is equivalent to that obtained for EC/LiPF₆, with a main band at 845 cm⁻¹, associated with free ions, and the bands at 838 and 852 cm⁻¹ are associated with ion pairs. The infrared study confirms our previous assumption on the basis of NMR investigation and shows that the ionic species are not fully dissociated.

Macroporous Membrane. The PVdF membranes obtained by phase inversion have a well-defined and reproducible porous structure. Figure 4 shows the SEM (scanning electron microscope) photographs of the membrane, where porosity is close to 70% with a homogeneous pore diameter, measured by mercury porosimetry, centered on 0.64 μm . The membrane formed an interconnected porous volume, where the electrolyte is likely to flow free as in a pure liquid phase.

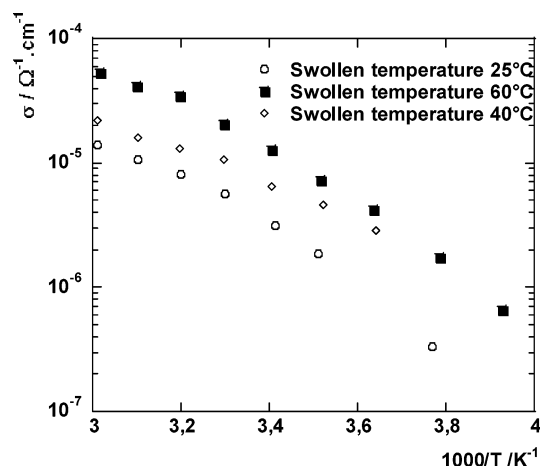


Figure 5. Conductivity comparison of dense PVdF membrane swollen by EC/DMC/DEC (2/2/1) + 1 M LiPF₆ electrolyte at different swollen temperatures.

Conductivity. Figure 1 shows the Arrhenius conductivity plot of the macroporous PVdF separator filled by the ternary electrolyte compared to that of the liquid electrolyte free of separator. Great attention was paid to the reliability of conductivity measurements, namely, (i) accuracy, using low-diameter electrodes, and (ii) reproducibility, carrying out measurements on four macroporous membranes. Thus, for instance, a conductivity of 3.1×10^{-3} S/cm was obtained at 21 °C, with an accuracy of $\pm 3 \times 10^{-4}$ S/cm.

The shapes of the conductivity curves for the liquid electrolyte alone and the same ones filling the macroporous PVdF are identical on the whole temperature range explored (−20 to +60 °C).

The decrease in apparent conductivity induced by the macroporous PVdF is 3.6 at every temperature. Assuming that the porous separator is not swollen by the electrolyte (for example, using a Celgard separator), the conductivity loss is generally associated, on one hand, with the reduction in the effective surface of the electrode. On the other hand, the effective way for the conduction to be defined is only by the interconnected network of pores; this one can be increased by a ratio, named tortuosity, compared to the geometrical distance between the two measured electrodes. If separator such as Celgard has very poor interaction both with the salt and the solvents of the liquid electrolyte, the situation may be different with a polar polymer such as PVdF and a contribution to the global conductivity may be expected from the swollen PVdF membrane. However, the high crystallinity (60%) of macroporous PVdF should limit its swelling and conductivity.

As has been shown in ref 10, for the macroporous membrane the swelling time is very short and the intercore swelling of PVdF membrane is quasi-immediate. To check whether or not the contribution of swollen PVdF to the global conductivity of the set macroporous membrane + liquid electrolyte is negligible, conductivity measurements were performed on dense PVdF membranes. The dense membranes were swelled, at various temperatures, in the ternary electrolyte up to the swelling equilibrium. The sorption kinetics of the carbonate solvents, their mixtures, and the solvent–salt mixtures in dense PVdF were soundly investigated and already reported.¹² In accordance with our previous data,¹² the dense membranes were swelled in the ternary electrolyte much longer than the time required for the equilibrium. In Figure 5 are gathered the conductivity plots obtained on swollen dense membranes. The conductivity increase with the temperature used to swell the PVdF membrane

TABLE 2: Measured and Calculated Conductivities of the Macroporous Membrane Swollen by EC/DMC/DEC (2/2/1) + LiPF₆ (1 M)^a

<i>T</i> (°C)	σ_{calc} (S·cm ^{−1})	$\sigma_{\text{calc}}\xi$ (S·cm ^{−1})	σ'_{exp} (S·cm ^{−1})	$\sigma'_{\text{exp}}/\sigma_{\text{calc}}$	$\sigma'_{\text{exp}}/\sigma_{\text{calc}}\xi$
30	1.45e^{-2}	8.5e^{-3}	5.5e^{-3}	0.4	0.7
60	2.16e^{-2}	1.3e^{-2}	8.5e^{-3}	0.4	0.7

^a ξ : dissociation degree.

is essentially due to the increase in the amount of electrolyte incorporated in the membrane.¹¹ But whatever the swelling temperature, the conductivities remain very low, the best conductivity reaching 6×10^{-5} S/cm at 60 °C, i.e., 2 orders of magnitude lower than those measured using the macroporous PVdF membrane. These low conductivities may be related to (i) the poor salt incorporation in PVdF membrane and (ii) the poor amount of electrolyte uptake. Indeed, studies on the swelling equilibrium but, also, on the composition of the dense PVdF membrane, were carried out¹¹ and showed the low salt concentration present in the membrane. Thus a salt concentration of 0.2 M is obtained in the swollen membrane from a molar concentration in the swelling solution. This results from the bad affinity, highlighted by spectroscopic studies, between PVdF and lithium salt.^{29,30} This low salt concentration may, to some extent, explain these low conductivities.

From these results, the contribution of the swollen intercore PVdF to the conductivity of the macroporous membrane can obviously be neglected. So, we may assume that in the macroporous membrane, the decrease in the effective surface of the electrode contributes by a factor 1.4 to the global conductivity decrease.

PGSE NMR. To explain the conductivity decrease by a factor of 3.6, much higher than 1.4, induced by the incorporation of the macroporous PVdF separator, PGSE NMR was performed on the macroporous PVdF filled by the liquid electrolyte. The kinetic study carried out on a dense PVdF membrane enables us to determine the swelling kinetics of PVdF in the macroporous membrane.¹² The equilibrium times, determined using the physical characteristics of our membrane and the diffusion coefficient measured in dense PVdF membrane, are as low as 1 or 2 ms, depending on the temperature. The macroporous membrane was swollen more than 1 h in the electrolyte before the preparation of the sample, a swelling time much longer than the equilibrium time.

Kataoka et al.³¹ performed investigations on macroporous PVdF by the same technique and observed two components of the diffusion process, which means that two discrete regions are present in the initial state. After a long stabilization time of the sample, only a single component of diffusion was observed. This suggests that the gel reaches equilibrium. Their conclusion is that the conduction mechanism in the macroporous membrane, obtained by phase inversion, is controlled not by the liquid electrolyte filling the porosity but by the polymer-rich region swollen by the electrolyte.

This paper clearly disagrees with this conclusion, as the conductivities of dense PVdF membrane swollen by the electrolyte are insignificant.

In addition for all the nuclei (Table 2), only one diffusion process is observed. It is beyond doubt that this single diffusion process is related to the diffusion in pores. This conclusion is supported by (i) the poor amount of electrolyte swelling PVdF in the macroporous membrane,¹¹ (ii) the negligible contribution of swollen PVdF phase to the conductivity, and (iii) the low diffusion coefficients of the nuclei in dense PVdF membrane.

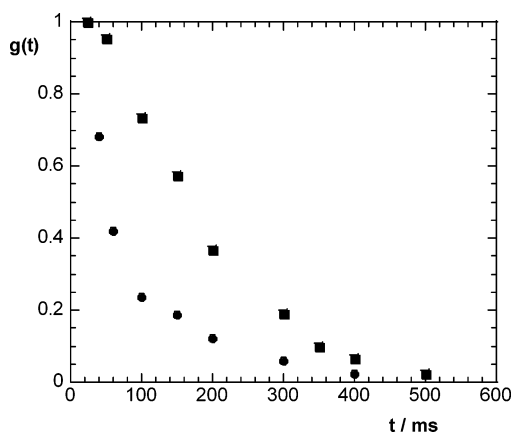


Figure 6. The time dependence of the transverse nuclear magnetization, $g(t)$, of the solvent protons (●) in the macroporous membrane and (■) in liquid electrolyte at 300 K.

Indeed we did not succeed in measuring the diffusion coefficients in a dense PVdF membrane swollen by the ternary electrolyte.

The diffusion coefficients of ^7Li , ^{19}F , and ^1H (solvent) are lower than the corresponding diffusion coefficients reached in the liquid electrolyte. Figure 6 shows, at $T = 300\text{ K}$, the normalized $g(t)$ of the protons in the macroporous membrane and liquid electrolyte. The faster decrease of $g(t)$ of the protons in the macroporous membrane with respect to the protons in liquid electrolyte indicate that the mobility of the solvents in the macroporous PVdF is more constrained than in liquid electrolyte free of separator. These two measurements, ^1H diffusion coefficient and ^1H $g(t)$, are in accordance with a viscosity increase in the porous media. Contrary to our previous report,³² the magnitude of mobility decrease is not the same for anion and lithium. Indeed the decrease in the diffusion coefficient is more notable for the lithium than for the solvents and the anion, whose diffusion coefficients are very close in the macroporous membrane. As a consequence, the cationic transference number t^+ , calculated from the diffusion coefficients, drops with respect to the liquid electrolyte free of a separator. The t^+ value, 0.26, is constant between 30 and 60 °C.

The use of a macroporous PVdF membrane decreases significantly both the mobility of all the electrolyte constituents and the cationic transference number. This effect might be related to a restricted diffusion process. Indeed the size of the diffusion region should be smaller than the total diffusion distance, the apparent diffusion coefficient then being decreased as compared to the free diffusion process. This does not occur in our macroporous separator as the polymer does not induce any blocking effect even when the migration distance, estimated from the diffusion time, is $5\text{ }\mu\text{m}$ ($t = 60\text{ ms}$), i.e., much higher than the average pore diameter ($0.64\text{ }\mu\text{m}$). In fact, we measured the diffusion coefficient of the cation (Li^+) at $T = 333\text{ K}$ for two values (40 and 60 ms) of the time interval between the two magnetic field gradient pulses, the other parameters being constant. We did not observe significant variations between the values of the diffusion coefficient measured. It could be noticed that the attenuation of the spin-echo vs the amplitude of the magnetic field gradient is strictly monoexponential, which excludes a distribution of diffusion coefficients.

Studies performed on swelling ability, swelling selectivity, and physical transformation of a PVdF membrane in the presence of electrolyte showed good affinity of PVdF with the solvents but not with the salt in accordance with others

publications.^{30,33} The reduction of the displacement of solvents through the pores may be related to an increase of viscosity which can be due to (i) the interactions of PVdF/solvents, (ii) the increase in salt concentration, and (iii) a modification in the salt dissociation. This deceleration of solvents involves a reduction in the mobility of the ionic species. Due to the solvation ability of the solvents versus lithium cation, the cation diffusion coefficient is approximately decreased by the same factor. Due to its poor interactions with PVdF and carbonate solvents, the diffusion coefficient of the anion is less affected. These evolutions of $D(\text{Li}^+)$ and $D(\text{PF}_6^-)$ induce a decrease, vs liquid electrolyte, of the cationic transference number, while a paper¹⁷ dealing with PVdF gelled electrolyte reported an increase of t^+ .

As previously noted, the concentration of LiPF_6 in the PVdF membrane is very low. So, the salt concentration in the liquid electrolyte filling the pores increases. Using the data about the salt concentration and the amount of electrolyte swelling PVdF, a salt concentration of 1.1 M could be determined in the electrolyte present in the pores. This increase in salt concentration is of course in accordance with an increase of the electrolyte viscosity but is not enough to explain the clear diffusion coefficient decrease.

The latter might be related to solvent interactions both with the polymer and the salt. The calculated volume of a single layer of adsorbed solvent on the surface of the membrane can be estimated from simple geometrical considerations. It represents only 0.5% of the volume of solvent included in the pores and is not enough to explain the decrease of the diffusion coefficients. However, it may be assumed on one hand that the specific surface might be much more important than the geometric one and on the other hand that the interaction of PVdF/solvents may impact on more than a single layer of solvent.

To determine the influence of the interactions on the diffusion slowing down, more investigations should be performed, e.g., comparison with other separators and selection of other solvents and salts. Thus, the use of electrolyte solvents with a poorer ability to swell PVdF, i.e., a lesser affinity with the polymeric phase, limits the conductivity drop in macroporous PVdF.³² Solvents with a high affinity may decrease the effective electrode surface. Indeed it may be assumed that the greater the swelling is, the smaller the porosity is and the smaller the effective electrode surface is.

The values of σ_{calc} (NMR measurement) and σ_{exp} are given in Table 2. σ_{exp} (determined by impedance spectroscopy) was modified by multiplying the value by 1.4 (noted σ'_{exp}), to correct the effect of the surface decrease related to the presence of poor conducting zones. The ratio $\sigma'_{\text{exp}}/\sigma_{\text{calc}}$ is lower than that obtained for the corresponding liquid electrolyte ($\sigma'_{\text{exp}}/\sigma_{\text{calc}} = 0.4$ vs 0.6). This difference may be related to (i) an increase of salt association, (ii) an additional effect of the swelling on porosity and thus on the electrode surface, and (iii) a tortuosity effect.

Salt Association. An increase of salt association might be expected from the slight increase—10%—of the salt concentration in the liquid electrolyte, but also from the modification of the solvent composition due to PVdF/solvent interactions. Swelling ratios and selectivity of the PVdF membrane previously studied¹¹ show for the ternary mixture an impoverishment in DMC and EC compared to DEC in the liquid electrolyte filling the pores. Yet, this modification of the composition is low. Then a low decrease of the dielectric constant could be expected, inducing a small increase of ionic association. This ionic

association is not enough to explain the difference between σ_{calc} and σ'_{exp} . The ionic association must therefore be taken, in first approximation, equal to the value determined in the liquid electrolyte.

Swelling Effect. The swelling of the membrane which might reduce porosity and thus electrode effective surface cannot be sufficient, also, to explain the residual 0.7 factor observed between σ'_{exp} and $\xi\sigma_{\text{calc}}$ ($\sigma'_{\text{exp}}/\sigma_{\text{exp}}$ corrected with initial 1.4 surface electrode reduction; $\xi\sigma_{\text{calc}}$ takes into account the ionic association observed in the liquid electrolyte).

Tortuosity. If ionic association and swelling effects on effective surface electrode allow the gap between calculated and experimental values to be partly explained, both explanations are insufficient. One may invoke a tortuosity factor due to the increase of the distance covered by the ionic species through the pores of PVdF membrane probably around 1.5.

In addition the influence of pore sizes was evaluated through conductivity measurements.³¹ For the same porous volume, it was observed that conductivity decreases with the decrease of pore diameters which might result from an increase in tortuosity and/or from interactions on a greater polymer/solvent interface.

Conclusion

As a conclusion we can first try to summarize the different factors responsible of the conductivity decrease (decrease factor, 3.6) observed when the macroporous separator is introduced in the liquid electrolyte. First, a large part of this decrease (but still <2.1) may be attributed to the initial geometrical characteristics of the membrane, namely, its porosity, that decreases the effective electrode surface (1.4) and introduces a tortuosity lower than 1.5. Then, a part of this conductivity fall may be attributed to an increase of the solvent viscosity, which may be due to interactions between solvents and PVdF, and cannot be connected to a wall blocking effect.

A good affinity between the PVdF membrane and solvents is thus a pledge of good electrochemical performance because of a good wetting of the pores. However NMR and conductivity data indicate that, in the same time, this affinity can also decrease significantly the ionic mobility. Moreover, the decrease in cation mobility is more detrimental toward lithium battery application.

Acknowledgment. Acknowledgments to Ministère de l'Economie des Finances et de l'Industrie for financial support and at our partners Alcatel-Saft and Totalfina. The corresponding author wishes to repair his lapse of memory at the time of the acknowledgments of the publication entitled "Nanocomposite Polymer Electrolytes Based on Poly(oxyethylene) and Cellulose Nanocrystals" published in this Journal (2004, 108, 10845–

10852). The corresponding author thanks M. Nicolas Glandut and M. Jean-Paul Diard for their fruitful discussions and helping in whiskers electrochemical characterization.

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