Macromol. Symp. **2003**, *200,* 101—110

Study of the Interaction Polymer/Organic Solvents/Salt in Microporous PVdF Separator for Lithium Batteries

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Summary: Interactions between microporous PVdF and polar liquid electrolytes have been investigated. PVdF separators are an attractive alternative to microporous apolar polyolefins, such as polyethylene, whose poor wetting by these electrolytes induces a significant resistivity increase in lithium batteries. The swelling study of polymer/electrolyte interactions has shown that the resistivity increase induced by microporous PVdF is moderate and will enable the electrolyte composition to be optimized. Existence of a shut-down effect is an asset for the battery safety.

Keywords: gels; microporous separator; polymer electrolyte; PVdF; swelling

Introduction

Despite improvements (i) in specific energy and power and (ii) in lifetime and reliability, progress in light rechargeable batteries remains very important for portable electronics, like computers or cellular phones, particularly with the growing interest of end-users for micro fuel-cells. Although the technological problems induced by the miniaturization of PEM fuel cells are not completely solved, they are very attractive for end-users since the recharge, i.e., the fuel refill, is almost instantaneous. The main specifications of lithium batteries intended for use in electronic applications are high specific and per volume energy and power, even at low temperature, and they therefore require highly conductive electrolytes. In addition, special attention must be paid to cost, lifetime and safety of the batteries. As the size decrease of cellular phones would be determined by a decrease in thickness rather than in surface area, the present day trend is to use flexible thin batteries. As cellular phone batteries must operate even at –20°C, the electrolytes consist mainly of a solution of a lithium salt in a liquid mixture of aprotic solvents, and therefore dry (free of liquid solvents) salt/polymer complexes, well-

DOI: 10.1002/masy.200351010

adapted to thin and flexible batteries, cannot be used. A microporous polyolefin separator, filled with a liquid electrolyte is used in most commercial batteries. It must provide sufficient thermal and mechanical stability, and a wide enough electrochemical stability window. These separators, apolar polyolefins: polyethylene or (and) polypropylene, have a major drawback, namely their poor affinity for polar organic electrolytes. This results in a sharp resistivity increase with respect to the pure liquid electrolyte. In addition, such separators do not allow the electrolyte + electrode set to be shaped into thin and flexible batteries. Another approach deals with the use of gelled electrolytes. The polymer matrix must interact sufficiently with the liquid electrolyte to ensure a high swelling rate, hence a high conductivity, and must present a wide electrochemical stability window. Proposed earlier by Feuillade et al.,[1] these gelled polymer electrolytes have been investigated less than pure polymer electrolytes. Thus, most of the gels reported remain based on polyacrylonitrile PAN,[2,3] PVdF-co-HFP[4,5] or poly(oxyethylene).[6,7] We recently proposed[8,9] to prepare networks from random copolymers of methacrylonitrile, whose electrochemical stability in reduction is improved with respect to PAN. This paper deals with an electrolyte which might be considered as intermediate compared to the previous ones. Indeed, due to its porosity, microporous PVdF filled with organic electrolyte is close to polyethylene/polypropylene, while, owing to its polarity and its affinity with most liquid solvents, PVdF has similarities with gelled electrolytes. The aim of this paper is to study PVDF/solvent/salt interactions, mainly performed on dense polymer slabs.

Experimental

Microporous PVdF-membrane was prepared as previously described,[10] while dense PVdF was obtained by hot-pressing PVdF powder (205°C) and fast tempering. Aldrich solvents were used for tests. Merck battery grade solvents and $LiPF_6$ were used for the electrolytes and stored in a glove-box under argon. The electrolyte composition inside PVdF gels was calculated using ^{1}H and ^{19}F NMR (Brucker AC 200, $(CD_3)_2CO$). The swelling ratios were obtained by differential weighing. Experiments with salt were done in Ar flux or in a glove-box. For kinetics, the slab must be very thin, thickness being neglected compared to surface. The melting and glass transition temperatures, Tm and Tg, were studied using a TA DSC2920 CE (modulated, oscillation period 60 s, amplitude: ±1°C) and a Netzch STA 409 DSC. X-ray scattering spectra were recorded on a Siemens D500 goniometer using Cu-K$_{\alpha 1}$ radiation at 0.15406 nm. IR spectra were recorded on a Nicolet 720 FTIR (32 scans, ±4 cm^{-1}). DMA measurements were made in Ar flux, on a Rheometrics RSA2, in traction mode, in the linear viscosity range of the sample (1 Hz 3°C/min step). The temperature range was –120°C +10°C and sample dimensions were 1×30×5mm. The conductivity of the liquid electrolytes was measured using a Tacussel cell with a thickness/surface geometrical factor close to 1 cm^{-1}. Conductivity measurements on polymer electrolytes were made in button type coin cells (CR 2430) with a stainless steel electrode of diameter 6 mm. Both were carried out in Ar by impedance spectroscopy over the frequency range 5 Hz -13 MHz, using an HP 4192A analyser.

Results

PVdF behaviour was investigated separately with each carbonate (diethylcarbonate -DEC-, dimethylcarbonate -DMC- and ethylene carbonate -EC-), with salt-free carbonate mixtures, and with molar solutions of the lithium salt ($LiPF_6$). Indeed, interactions have non negligible consequences on the system. First, sufficient interaction is required in order to obtain good wetting of the membrane by the solvents. Second, too strong interactions must be avoided as they can (i) lower the conductivity by decreasing ionic mobility and modifying the electrolyte amount and composition inside the porosity, (ii) lower the thermal and mechanical stability because of too huge swelling and (iii) damage the membrane and the electrode/membrane contact because of swelling.

Lowering of the Ionic Conductivity

Figure 1 shows that the use of this PVdF separator results in a resistivity increase (by a factor 3.58) with respect to the pure liquid electrolyte. PFGNMR[11] allows a decrease of both cation and anion mobility observed when the electrolyte fills the separator and that solvent mobility is also decreased. Moreover these experiments show that this mobility reduction is not due to a wall effect blocking the ionic species but to the solvent/polymer interaction which, coupled to salt solvation by the solvents, will reduce the mobility of the ion. This is confirmed by the fact that changing the solvent mixture changes the loss factor: with mixtures with lower interaction the loss factor is smaller (Table. 1).

Table 1. Swelling ratio of the electrolyte compared to the conductivity loss factor.

	DEC/DMC/EC	DEC/EC
Mass swelling ratio	1.28	1.22
Loss conductivity factor	3.58	2.45

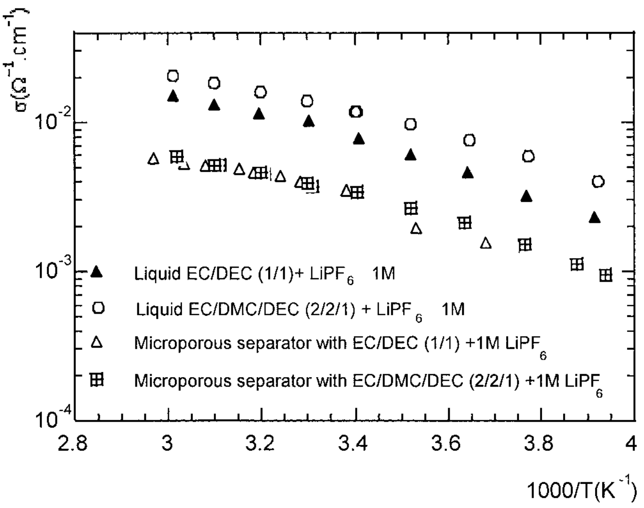

Fig. 1. Ionic conductivity for a $LiPF_6$ 1M electrolyte with and without separator.

The conductivity decrease can thus be explained by solvent/PVdF interaction and by the reduction of the effective electrode surface. There is no, or at least low, tortuosity in this electrolyte, probably because of the sufficiently wide pores (0.64 microns) and porosity (70%). Although these interactions induce a lowering of conductivity, the conductivity remains much higher than that of the electrolyte + microporous polyethylene set.

Thermal Stability

A gelled membrane will melt at a lower temperature than the neat polymer. T_m reduction depends on swelling ratio and on solvent nature. As given by the Gibbs-Thomson equation, the more solvent there is, the lower the gel T_m will be. Moreover the reduction will be favoured by smaller solvents and those whose affinity for the polymer is the best. This is clearly the case for our system, where the smaller and better solvents of PVdF such as DMC and EC have a stronger effect[12] (Fig. 2). For microporous PVdF already filled with the ternary electrolyte and heated in the presence of additional electrolyte, T_m drops from 141°C to 80°C and pores are plugged up as the temperature is increased.

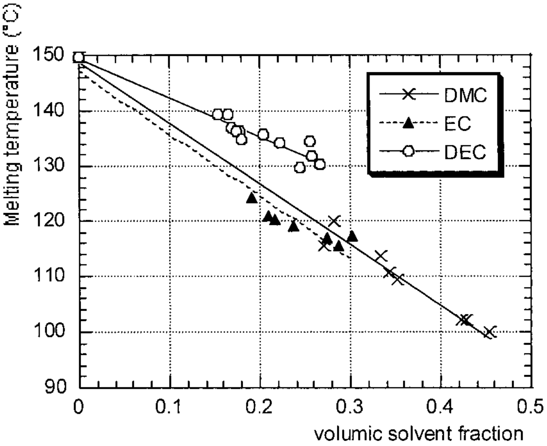

Fig. 2. Gel melting temperature *vs* volume fraction for different solvents.

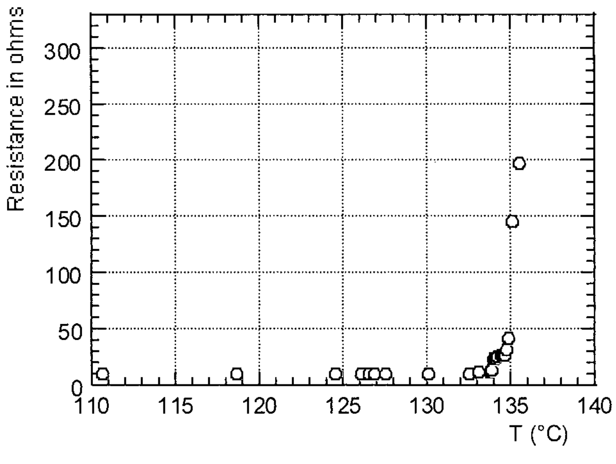

Fig. 3. Variation of resistance with temperature of microporous PVdF electrolyte.

As a consequence, there is a sharp increase in resistivity (Fig. 3), which results in a beneficial shut-down effect, preventing the battery from overheating.[10]

Mechanical Stability

The mechanical properties of the gel are damaged compared to those of the neat polymer. Due to lower interactions between chains and generation of an additional free volume, chain reptation is easier and the glass transition occurs at a lower temperature (Fig. 4). Depending on the free volume generated by solvents and interactions between molecules, the lowering can be sharper : the free volume created by linear carbonates that are less viscous and have more spatial conformations than a plane rigid EC molecule is thus higher.[12]

A sharp reduction of the elastic modulus, E, which can result from the worse chain cohesion in gel and from some other specific effects, such as crystalline modifications (orientation, ratio), was also observed.

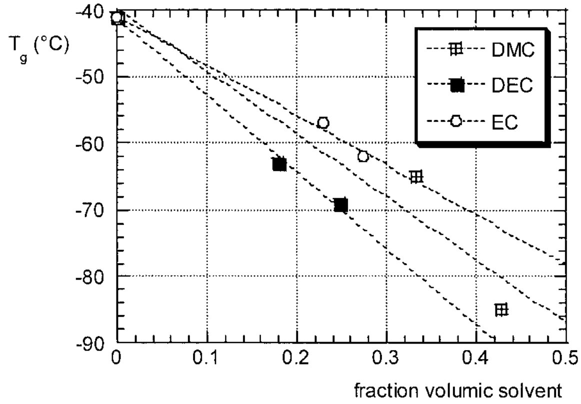

Fig. 4. Dependence of Tg on solvent volume fraction for different solvents.

Degradation

Some degradation exists, as proved by some hysteresis, which affects the swelling behaviour of dense membranes. Thus a membrane submitted to a first swelling will no longer swell as previously, after solvent evaporation and renewed swelling (Table 2).

Table 2. Swelling hysteresis. Some swelling ratios and kinetic data.

	Diffusion coefficient in DMC at 60°C D (cm^2s^{-1})	Mass swelling ratio in DMC at 25°C
First swelling at 25°C	1.7 10^{-8}	1.19
After first swelling at 60°C	5.2 10^{-8}	1.275

Some macroscopic fissuring was observed in the sample surface for high swelling ratios. Nanofissuring might occur before this visible degradation but classical SEM observations or porosity measurements were unsuccessful in characterizing them. Hysteresis in swelling is however in agreement with this assumption. Disorientations of the alpha crystalline phase, proved by the relative intensity modification of X-ray alpha peaks, were observed after swelling occurred. No change in crystalline ratio was indicated. The melt sample viscosity was reduced by a factor close to 1.25 after previous swelling in DMC at 60°C. This might be related to partial disentanglements in the amorphous phase.

Swelling and Selectivity[13]

At 60°C the mass swelling ratio in the electrolyte is not too high and will be compatible with the application. Probably owing (i) to a poor polymer/salt interaction and (ii) to strong EC/$LiPF_6$ complexes, DEC and DMC penetration is favoured in the presence of lithium salt. The small polymer content in the microporous membrane (30%) associated with its moderate swelling ratio, should however prevent a significant increase in EC in the electrolyte which could induce crystallisation at low temperature.

Prediction of swelling ratios, however, is an important challenge because swelling has a strong effect on system performance. Prediction is a very hard problem. First, the system consisting of polar solvents and a semi-crystalline polymer reaches the limit of the Flory-Huggins theory. Second, some of the mixtures used exhibit a synergetic effect, i.e., if the affinity between solvents in the mixture is bad ($\chi_{s1s2}>0$), there is overswelling (EC/DEC or EC/DMC) (Fig. 5). Some analogous synergetic effects are observed for swelling kinetics as far as diffusion coefficients and activation energies are concerned (Table. 3). In the case of DMC/DEC mixtures, no synergy connected with solvent/solvent interaction occurs and the value of χ_{s1s2} is close to zero.

Table 3. Mixture effect on diffusion coefficient D at 60°C and activation energy E_a for the Fickian part of the sorption curve.

	DEC	EC	DMC	DMC/EC	DEC/EC	DEC/DMC	EC/DMC/DEC
D /cm^2s^{-1}	2.10^{-9}	4.10^{-9}	10^{-8}	8.10^{-9}	$2.2.10^{-9}$	$3.9.10^{-9}$	5.10^{-9}
E_a/kJ mol^{-1}	103	87.4	56.7	55.8	56.3	49.3	47.4

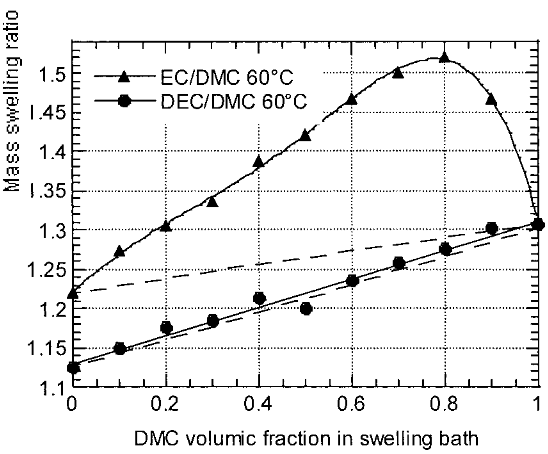

Fig. 5. Swelling ratio versus solvent fraction in equal volume binary solvent mixtures.

The major problem originates from the incorporation of salt, which completely modifies the swelling behaviour (ratio, selectivity (Fig. 6) and kinetics).

Swelling by mixtures based on EC regularly decreases as salt concentration increases, while the evolution with salt concentration of DEC and DMC swelling curves present a maximum. The shape of the sorption curve also changes: it is no longer an S-shaped sorption curve, as in salt-free solvent mixtures, but a two stage sorption.

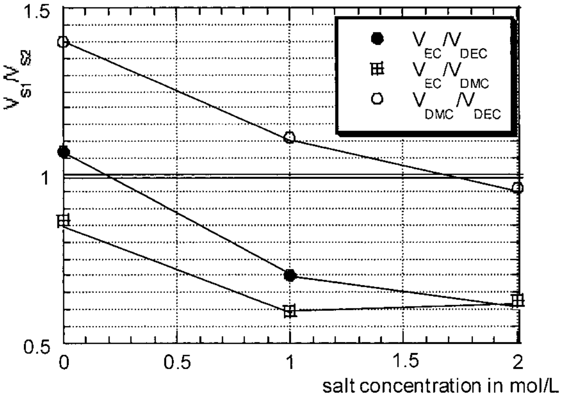

Fig. 6. Solvent volume ratios in gel versus salt concentration in the swelling bath.

Conclusion

This study has shown that, due to good wetting of the porous volume by aprotic polar electrolytes, the use of microporous PVdF separators does not result in a large increase in resistivity. Conductivity data and Pulsed Field Gradient NMR show that in such separators the tortuosity is close to 1. Swelling investigations will allow the electrolyte mixture to be optimised, while a shut-down effect, which improves the battery safety, was noticed.

Despite the fact that the aim of this research deals with the improvement of lithium-ion polymer batteries, the basic research aspects were not neglected. In this multidisciplinary research field, polymers often allow battery performances to be improved in terms of safety, electrochemical stability, thickness and flexibility. However, such approaches of interactions between polar solvent mixtures and semi-crystalline thermoplastic polymer may in turn shed a new light on complex liquid / polymer interactions.

Acknowledgments

We are grateful to the Ministère de l'Economie des Finances et de l'Industrie for financial support and to our partners Alcatel-Saft and Atofina.

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