^{7}Li and ^{19}F diffusion coefficients and thermal properties of non-aqueous electrolyte solutions for rechargeable lithium batteries

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Abstract

In this paper, electrolyte solutions of ethylene carbonate (EC) and ethylene methylene carbonate (EMC) with different salts as $LiPF_6$, $LiBF_4$ and $LiN(SO_2C_2F_5)_2$ were prepared and characterized using Pulsed Field Gradient (PFG) NMR and DSC. Cation transport numbers, τ^+, ranging between 0.37 and 0.49 were obtained. The maximum value of 0.49 was obtained in the case of a 0.5 M solution of $LiBF_4$ in 2:8 EC:EMC. The DSC data suggest that the increase of EMC stabilizes the electrolyte solution towards low temperature, and that a 2:8 EC:EMC ratio assures good stability at low temperature to the electrolyte solution. While $LiN(SO_2C_2F_5)_2$ seems to score the best in terms of low temperature stability, $LiPF_6$ may offer the best cost/performances compromise. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Nowadays, the research on rechargeable lithium batteries involves a big effort directed to both materials development and new production technologies. Among the most promising polymer electrolytes, a relevant position is occupied by the so-called gel electrolytes [1], in which a non-aqueous electrolyte solution is trapped into appropriate host polymers like poly(acrylonitrile) (PAN), poly-(methyl metacrylate) (PMMA), or poly(vinylidene fluoride/hexafluoropropylene) (PVdF-HFP). In this frame, many efforts are nowadays directed towards the optimization of non-aqueous electrolyte solutions [2–4]. Alkyl methyl carbonates and salts as lithium bisperfluoroethanesulfonimide ($LiN(SO_2C_2F_5)_2$) are conveniently employed to obtain promising electrolytes for this application [5].

A very important point for the applications in the next future is the need to increase the transport number of the polymer electrolytes. To this aim, a good knowledge of the electrolyte solution behavior is mandatory, and the Pulse Field Gradient (PFG)-NMR technique is very useful to achieve this target [6]. With this technique, in fact, it is possible to measure the diffusion coefficients of both the anions and the cations, therefore determining the cation transport numbers. In the present work, the diffusion coefficients of lithium and fluorine will be measured for different electrolyte solutions based on different ratios of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with different concentrations of three lithium salts: $LiPF_6$, $LiBF_4$ and $LiN(C_2F_5SO_2)_2$. The cationic transport numbers will be determined.

On the other hand, the thermal stability of the electrolyte is also a very important parameter for technological applications. Actually, in fact, lithium batteries are required (or they will be soon) to operate over the same temperature range on which the electronic components do work, i.e., from −40 to 85°C. With this in mind, our solutions have been also investigated by Differential Scanning Calorimetry (DSC) in order to state their thermal stability chiefly below room temperature. In the following, we will discuss our results with the main target to understand what is the best compromise we can achieve between

Table 1

Samples

Salt	Conc. M/1	EC:EMC ratio	Cationic transport number τ^+ Li$^+$
LiPF$_6$	1.5	2:8	0.42
LiPF$_6$	1.2	2:8	0.42
LiPF$_6$	1.0	2:8	0.43
LiPF$_6$	0.8	2:8	0.42
LiPF$_6$	0.5	2:8	0.43
LiPF$_6$	0.1	2:8	0.42
LiPF$_6$	0.05	2:8	0.40
LiPF$_6$	0.02	2:8	0.37
LiPF$_6$	1.0	6:4	0.37
LiPF$_6$	1.0	4:6	0.40
LiN(C$_2$F$_5$SO$_2$)$_2$	1.0	2:8	0.48
LiN(C$_2$F$_5$SO$_2$)$_2$	0.5	2:8	0.43
LiN(C$_2$F$_5$SO$_2$)$_2$	0.1	2:8	0.47
LiN(C$_2$F$_5$SO$_2$)$_2$	0.05	2:8	0.45
LiN(C$_2$F$_5$SO$_2$)$_2$	0.02	2:8	0.42
LiBF$_4$	1.0	2:8	0.47
LiBF$_4$	0.5	2:8	0.49
LiBF$_4$	0.1	2:8	0.46
LiBF$_4$	0.05	2:8	0.45
LiBF$_4$	0.02	2:8	0.35

the thermal and transport properties of the electrolyte solution.

2. Experimental details

Electrolyte solutions with different EC/EMC ratios and different salts were prepared as reported in Table 1. All the operations were performed in a dry box.

PFG-NMR measurements were performed on an AL-PHA NMR-JEOL 500 MHz spectrometer using a stimulated pulse sequence [7]. The solutions were inserted in standard NMR tubes that were closed using a flame to avoid the contact with moisture. The data for ^{7}Li were acquired at a Larmor frequency of 194 MHz, with a 90° pulse of 11.50 μs. The data for ^{19}F were acquired at a Larmor frequency of 470 MHz, with a 90° pulse of 12.5 μs.

The DSC measurements were performed on a DSC220CU SEIKO Electronic Industry. Samples of 5 mg were inserted in aluminum pans, cooled down from 30°C to about −100°C at the rate of 5°C/min and then reheated at the same heating rate of 5°C/min.

3. Results and discussion

3.1. The NMR information

^{7}Li and ^{19}F NMR spectra were obtained on all the solutions reported in Table 1. As expected, a single peak was always observed for ^{7}Li. Concerning the ^{19}F for both LiPF$_6$ and LiBF$_4$ we found doublets which can be assigned to scalar J–J coupling between ^{31}P and ^{19}F, and between ^{11}B − ^{10}B and ^{19}F, respectively. In the case of LiPF$_6$, we obtained a symmetric doublet with a coupling constant, ^1J, of 750 ± 10 Hz, in agreement with the values usually observed for fluorine salts [8]. In the case of LiBF$_4$, we observed a strongly asymmetric peak due to quadrupolar relaxation effects [9], with a coupling constant $^1J = 70 \pm 5$ Hz. Concerning the ^{19}F of LiN(C$_2$F$_5$SO$_2$)$_2$ a double peak was also observed.

Fig. 1 show the diffusion coefficients, D, of ^{7}Li and ^{19}F for the three salts we employed, at an EC/EMC ratio 2:8. The first evidence is that the diffusion coefficients of ^{19}F are always higher than the ones of ^{7}Li, probably, because Li is coordinated by some molecules of solvent. All the curves, except the one of ^{19}F in LiBF$_4$, show a maximum
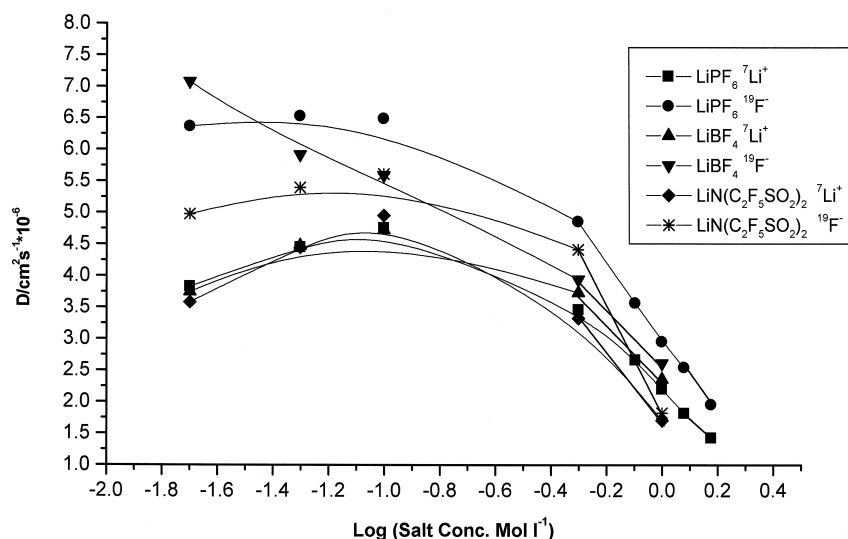

Fig. 1. PFG-NMR diffusion coefficients, D, of ^{7}Li and ^{19}F for the three salts we employed, at an EC/EMC ratio of 2:8.

against the concentration. However, all the diffusion coefficients score nearly the same at high concentration. The behavior of the lithium diffusion vs. concentration is similar for the three salts, which is quite expected since the solution and, as a consequence, the Li^+ salvation shell, are the same. In contrast, ^{19}F shows different behaviors, which is also quite expected since the anions have different dimensions. In particular, PF_6^- travels faster than $N(C_2F_5SO_2)^-$ and BF_4^-. This last anion also shows an anomalous behavior at low salt concentration.

The cation transport numbers, τ^+, are reported in Table 1 for all the samples we studied. In average, $LiN(C_2F_5SO_2)_2$ and $LiBF_4$ scores better than $LiPF_6$. The maximum value of the series, $\tau^+ \cong 0.49$, has been obtained for 0.5 M of $LiBF_4$ in 2:8 EC:EMC.

3.2. The DSC information

Fig. 2 shows the DSC thermograms below room temperature of 1 M $LiPF_6$, 1 M $LiBF_4$ and 1 M $LiN(C_2F_5SO_2)_2$ in 2:8 EC:EMC. The first two salts give origin to a complex pattern of crystallization/melting during the heating cycle. In contrast, $LiN(C_2F_5SO_2)$ behaves like a pure liquid, and therefore seems to be the best suited for

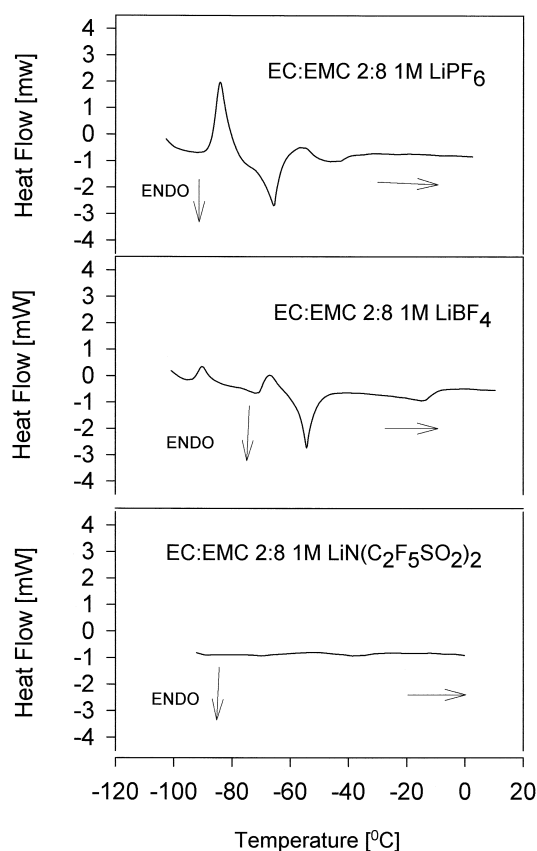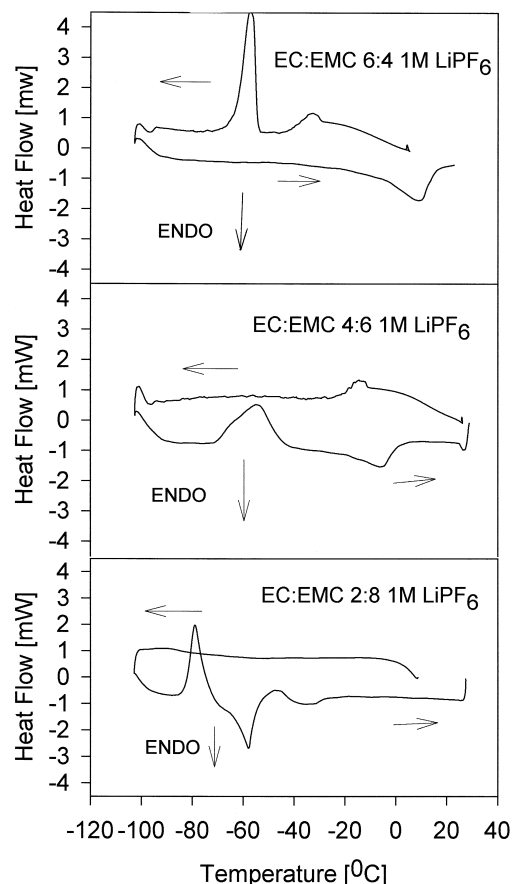Fig. 3. DSC thermograms of solutions with different $LiPF_6$ concentrations in 2:8 EC:EMC.

applications as the electrolyte at low temperatures, at least at a concentration of 1 M.

Let us now put our attention of $LiPF_6$, which is probably the most promising candidate as the electrolyte salt both from economical and safety points of view. Fig. 3 shows the DSC thermograms of solutions with different $LiPF_6$ concentrations in 2:8 EC:EMC. For salt concentrations up to 1.2 M, crystallization/melting patterns are again observed, which can be attributed to the solvent mixture by itself, to a solvent/salt complex, or to both of them. At a concentration of 1.5 M, $LiPF_6$ seems to hinder the crystallization process of the supercooled liquid. In fact, no thermal effects are observed. This behavior is similar to that of 1.5 M $LiN(CF_3SO_2)_2$ in 1:1 EC:PC [10].

Fig. 4 shows the thermal behavior of 1 M $LiPF_6$ solutions with different ratios EC:EMC. Here also, the cooling curves are shown. In the case of 6:4 EC:EMC, we have two exothermic peaks at $-20°C$ and at $-60°C$ when the sample is cooled and a wide melting endothermic above $0°C$ when the sample is heated. In the case of 4:6 EC:EMC, we have a small exothermic peak at $-10°C$ during cooling and two peaks during heating, the former one at $-60°C$ (exothermic) being related to a cold crystallization, and the latter (endothermic) again to the melting. Finally, in the

Fig. 2. DSC thermograms below room temperature of 1 M $LiPF_6$, 1 M $LiBF_4$ and 1 M $LiN(C_2F_5SO_2)_2$ in 2:8 EC:EMC.
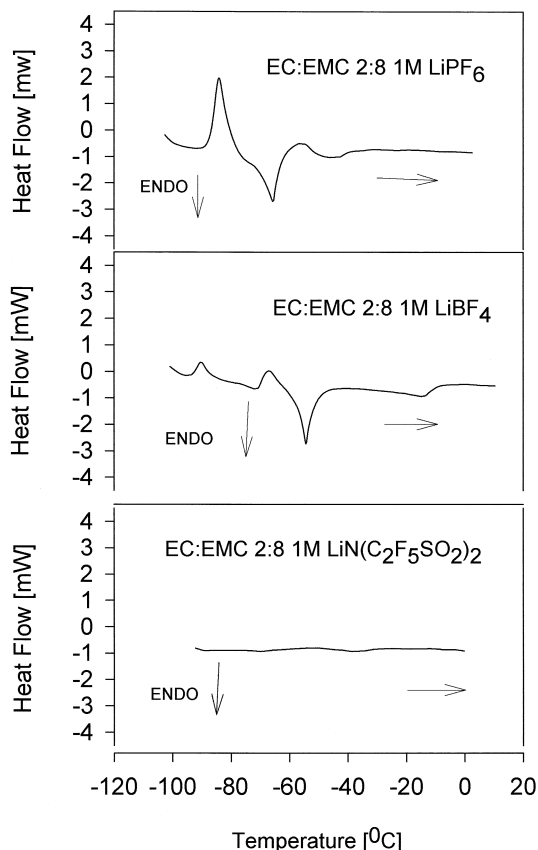
Fig. 4. DSC thermograms of 1 M LiPF$_6$ solutions with different EC:EMC ratios.

case of 2:8 EC:EMC, we have not any peak during the cooling cycle, whereas a clear pattern of crystall-ization/melting is observed during reheating. The relevant point here is that the increase of EMC stabilizes the liquid towards low temperature and therefore improves the be-havior of the electrolyte solution. From Table 1, we have τ^+ of about 0.42 for solutions with an EC:EMC ratio of 2:8 and a LiPF$_6$ content near 1 M.

4. Conclusions

In this paper, several electrolyte solutions with different volume ratio on ethylene carbonate (EC) and ethylene methylene carbonate (EMC) and different salts as LiPF$_6$, LiBF$_4$ and LiN(SO$_2$C$_2$F$_5$)$_2$ were prepared. Pulsed Field Gradient (PFG)-NMR technique has been used to deter-mine the ^{7}Li and ^{19}F diffusion coefficients and, as a consequence, the cation transport number, τ^+, which ranges between 0.37 and 0.49. The maximum value of 0.49 is obtained for a 0.5 M solution of LiN(CF$_5$SO$_2$)$_2$ in 2:8 EC:EMC.

The DSC data suggest that a 2:8 EC:EMC ratio assures good stability at low temperature to the electrolyte solu-tion. LiN(SO$_2$C$_2$F$_5$)$_2$ seems to score the best in terms of low temperature stability. However, if economical/techni-cal reasons push towards the use of LiPF$_6$, a concentration not lower than 1.5 M can offer good stability results.

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