

Influence of macromolecular additives on transport properties of lithium organic electrolytes

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Abstract

Composite electrolytes containing calix[6]pyrrole derivative as an anion complexing agent for I^- , BF_4^- and $CF_3SO_3^-$ anions are studied. The ^{19}F NMR and IR spectroscopy were used to check how the complexation of anions with calix[6]pyrrole derivative changes in different non-aqueous solutions characterized by various dielectric constants. The influence of cation (Li^+ versus Et_4N^+) was also tested. The conductivity data were collected for liquid systems based on polyethylene glycol dimethyl ether (PEODME) as a solvent and with varying concentrations of the supramolecular additive. The observed decrease of conductivity is attributed to the anion complexation. The conductivity and electrochemical properties of poly(vinylidene difluoride)-based (PVdF-based) calix[6]pyrrole-containing gel electrolytes were also tested. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Although lithium cells are a well-established commercial product, there is much place left for improvements concerning efficiency and stability of these devices. One of the problems that are subject of recent studies consists in enhancing cationic conductivity in the diverse electrolytes applied in the batteries: organic liquids, solid polymers and gels [1,2]. It is commonly known that lithium transference number, measured using ac impedance (as in ref. [3]) or dc polarization technique (as in ref. [4]) in typical organic solutions of applicable salts (like $LiBF_4$ or $LiCF_3SO_3$) in propylene carbonate (PC), ethylene carbonate (EC) or acetonitrile (ACN), or in lithium salts-poly(ethylene oxide) (PEO) complexes does not exceed 0.5 (e.g. [5–8]). Every step towards “lithium-only” conductance will improve the yield of a lithium cell, provided the overall ionic conductivity does not suffer. Several methods of improving cationic conductivity have been applied: introducing large and heavy anions of low mobility (e.g. [9,10]), immobilizing anions on the polymer chain (in the case of polymeric solid electrolytes) (e.g. [11,12]), lowering the mobility of the anions by complexing them with Lewis acid addi-

tives ($AlBr_3$, $SnCl_4$, boron compounds) (e.g. [13,14]), but none of them has given an ultimate solution until now. Another novel option is selective complexing of anions in the bulk of the electrolyte using macrocyclic molecules, analogous to crown ethers and their derivatives, which are well known as selective complexants for cations. Macrocycles containing electron-accepting groups in the inner ring have been studied lately and their ability to complex simple anions has been proven (e.g. complexes of urea derivatives of calix[4]arene and I^- or $CF_3SO_3^-$ [15,16] researched by Wiczorek’s group, cryptands and BF_4^- or ClO_4^- [17], or *meso*-octamethylcalix[4]pyrrole and F^- or Cl^- [18] studied by the team from Chalmers University of Technology).

Following this route, we have begun studies on electrochemical properties of PEO composites with macrocyclic compounds with larger macrocyclic hole. We decided to apply calix[6]pyrrole derivative (C6P), which is selective on larger anions (I^- , $CF_3SO_3^-$, BF_4^-) and, due to this, can be easier applied in PEO-based electrolytes. A significant change in the lithium transference number to values close to 1 was observed, accompanied by lowering of the overall conductivity by less than one order of magnitude [19]. The results seemed promising, because conductivity loss was related to the anion immobilization, when lithium cation conductivity remained the same or even higher. Following to this, we decided to continue our

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study by applying our additive to electrolytes with diverse structure and polarity: low M_w polyethylene glycol dimethyl ether (PEODME) as liquid analogue of solid PEO-based electrolytes, PVdF gels swelled with PC solution of several lithium salts and simple polar organic electrolytes based on PC, acetonitrile and methylene chloride. We tried to establish correlation between the complexing ability of the macrocyclic additive and these properties of the electrolytes that are related to battery applications.

2. Experimental

2.1. C6P synthesis procedure

C6P was synthesized from di(phenyl)di(pyrrol-2-yl)methane (synthesis proposed by Eichen and co-workers [20], improved [21] and adapted to 1/4-technical scale by us) as follows: 400 g of di(phenyl)di(pyrrol-2-yl)methane (synthesized by us) and 400 g of trifluoroacetic acid (Fluka) were dissolved in mixture of 32 kg of acetone (Brenntag, 99.5%) and 32 kg of 99.8% ethanol (courtesy of WIRASET Ltd.). Reaction mixture was stirred for 5 days at room temperature in the argon atmosphere. Then, the reaction mixture was cooled down to -5°C . After 12 h, the precipitate was filtered off and washed with 1000 ml of cold ethanol, and then dried, yielding 90 g (18%) of 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole.

Before application as the additive, the anion receptor was dried for above 200 h under high vacuum (diffusion pump). The temperature of the drying process was elevated up to 100°C . The weight loss of the product during the drying process was lower than 15%.

2.2. Samples preparation

All preparative operations were performed in an argon glove-box with humidity level under 3 ppm. The samples were either closed hermetically in appropriate vessels or left inside with the measurement devices connected to the glove-box.

ACN, CH_2Cl_2 (POCH, for DNA synthesis, water below 50 ppm) and PC (Fluka, puriss, anhydrous, $\geq 99.0\%$) were used as received. All salts (99% Et_4NBF_4 , 99.998% LiBF_4 , 99.995% LiCF_3SO_3 , 99% LiI) and low M_w PEODME (Aldrich, average $M_w = 500$ g/mol) were dried for over 72 h in temperatures up to 100°C under high vacuum (diffusion pump). For gel fabrication a PVdF-HFP copolymer (courtesy Atofina Poland) was used.

Two methods have been applied to synthesize the gel electrolytes: one-step (casting of the polymer material together with the electrolyte solution) and two-step (preparation of PVdF matrix and soaking in the electrolyte), giving similar results of ionic conductivity and mechanical strength. The C6P additive did not solve completely in the polymer-solvents solution nor in pure polar solvents used in typical organic electrolytes (like PC or ACN). Our gels contained a suspension of C6P in the polymer matrix and in the liquid phase.

2.3. Electrochemical measurements

For transference numbers determination in low M_w PEODME-based electrolytes the procedure originally proposed by J. Newman's group [22] and introduced by Ciosek et al. [23] to the liquid systems was applied. Three independent series of experiments were conducted—restricted diffusion (mean salt diffusion coefficient determination), concentration cell OCV measurements and symmetric cell polarization experiment. All operations were performed in an argon-filled glove-box.

The electrochemical stability of the electrolytes was studied by means of CV technique. Three electrode cells with Pt working, Ta counter and quasi-reference electrodes were filled either with liquid solutions or with PVdF gel prepared as soft jelly in order to establish good electrical contact.

All electrochemical experiments were performed on a PAR 273 (EG&G)–1255 FRA (Schlumberger) set and the results analyzed with a Power Suite (EG&G) or EQ 4.55 (B.A. Boukamp) software. Symmetric Li/gel electrolyte/Li cells were assembled for long-time impedance measurements. The ionic conductivity were measured by means of standard ac impedance technique in cells with stainless steel blocking electrodes.

2.4. NMR and FTIR equipment

Infrared absorption spectra were recorded on a computer interfaced Perkin-Elmer 2000 FTIR system with a wavenumber resolution of 2 cm^{-1} . The spectra were performed for samples placed in a cuvette with a 0.5 mm spacer. FTIR spectra were analyzed using a Galactic Grams Research software package using a Gaussian–Lorentzian function. NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer.

3. Results and discussion

3.1. NMR spectra

To omit the problem of deuterated solvents, we gave up ^1H NMR spectra measurements and performed ^{19}F NMR measurements for solutions of $(\text{C}_2\text{H}_5)_4\text{BF}_4$ and LiBF_4 in various solvents. Our aim was to investigate if the presence of C6P (1 mol per 2 mol of salt) may result in change of fluorine nuclei chemical shift, which should prove the presence of the anion–receptor interaction. We also tried to estimate the effect of Lewis acidity of a cation. A typical spectrum of ^{19}F NMR for a sample containing LiBF_4 is shown in Fig. 1. The presence of two peaks in the spectra should be explained by different shifts of two boron isotopes: ^{10}B and ^{11}B . All the values of maximum of higher peak are shown in Table 1.

The highest change of the chemical shift, 1.77 ppm, is observed for the LiBF_4 solution in the least polar solvent mixture ($\text{CH}_2\text{Cl}_2/\text{ACN}$ 9:1). As expected, the change of the chemical shift is lower in solvent mixtures with higher dielectric constant and donor numbers, which both have a significant influence on the salt dissociation and the equilibrium between the solvent-anion and receptor–anion interactions. Surprisingly, in the case of $(\text{C}_2\text{H}_5)_4\text{NBF}_4$, the changes in the chemical shift are not so

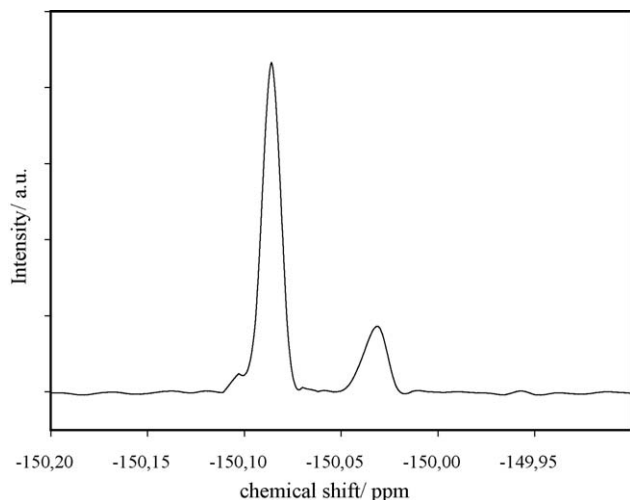


Fig. 1. The ^{19}F NMR spectrum of LiBF_4 in $\text{CH}_2\text{Cl}_2/\text{ACN}$ mixture.

significant. It was proved that complexation took place in a very similar environment [20]. These results suggest that C6P addition to the LiBF_4 solutions improves the salt dissociation. In the case of $(\text{C}_2\text{H}_5)_4\text{NBF}_4$, there was no significant effect on ^{19}F NMR chemical shifts due to better salt dissociation. For samples with high dielectric constant, we suggest that the complexation of the anions by the solvent particles (especially CH_3CN) inhibits the anion–receptor interactions.

3.2. FTIR

FTIR spectroscopy is widely used to analyze the receptor–ion (e.g. [24,25]), ion–ion (e.g. [26]) or ion–solvent (e.g. [27–29]) interactions. In the studied systems, the NH stretching vibration spectral region is of main interest. We compared FTIR spectra of C6P in solvents with various polarity: CHCl_3 and 1,2-dimethoxyethane (glyme) and also spectra of C6P/glyme and C6P/ $\text{LiCF}_3\text{SO}_3/\text{glyme}$ with the same C6P concentration (Fig. 2a and b). It can be clearly seen that the shape of the NH band differs depending on the solvent used. In the C6P/ CCl_4 solution, we observed a maximum of the peak at 3443 cm^{-1} (Fig. 2a) while in the C6P/glyme solution this band is split into two distinct contributions, with maxima at 3426 and 3260 cm^{-1} . However, these bands are in fact more complex and their deconvolution reveals presence of at least four peaks, with maxima at 3412 , 3424 , 3436 and 3459 cm^{-1} .

Additionally, in diglyme solution there are two weaker but broad bands, at 3315 and 3500 cm^{-1} , the former one correspond-

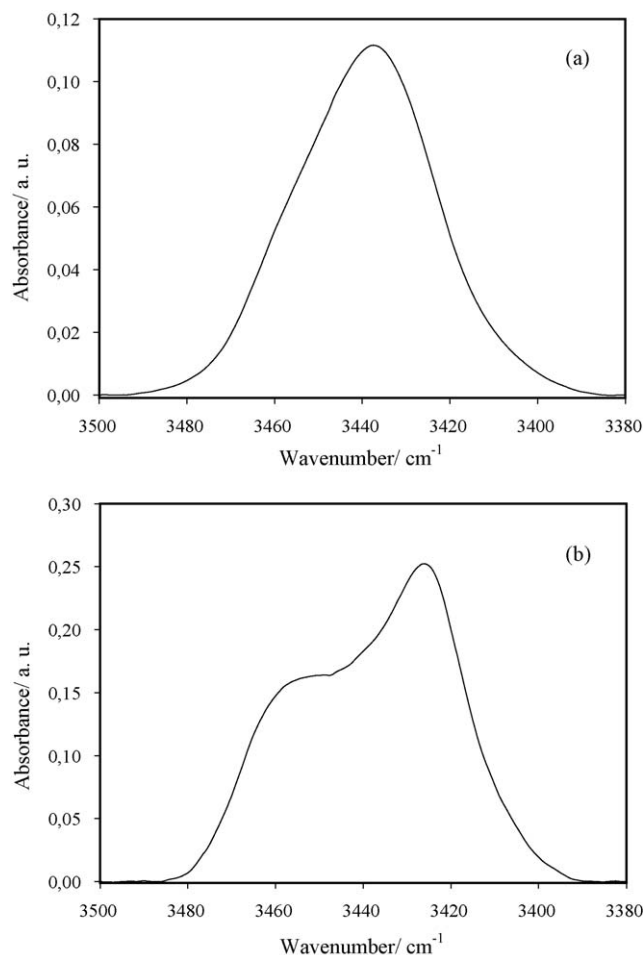


Fig. 2. A comparison of FTIR spectra of the C6P solution in CCl_4 (a) and glyme (b). Concentration of the C6P equal to 20 mmol/kg .

ing to H-bounded NH group, the latter to free NH groups. The same bands, but far less intense (in particular that at 3315 cm^{-1}) were found in the spectrum of C6P/ CCl_4 solutions. This indicates that in CCl_4 solution non-bounded NH groups predominate, while in the glyme solution a part of the NH groups can interact with solvent molecules.

Fig. 3 shows a comparison of the spectra of C6P/glyme and C6P/ $\text{LiCF}_3\text{SO}_3/\text{glyme}$ solutions with the same C6P concentration. As can be seen, the addition of the salt does not influence significantly the NH band shape. The only visible difference is the slightly lower intensity of the band at 3515 cm^{-1} for the salt containing sample.

3.3. Conductivity of PEODME- LiBF_4 -C6P composites

The conductivity values of PEODME-LiI-C6P composites are shown in Fig. 4.

Addition of calix[6]pyrrole derivative to the low M_w PEODME-LiI system leads to a decrease in overall conductivity of about one order of magnitude. Moreover, this decrease is observed only in samples with high salt concentration—in diluted samples the conductivity is almost the same for all series. The maximum conductivity for the system with an addi-

Table 1
 ^{19}F NMR chemical shifts (higher) of BF_4^- anion

Solvent	Chemical shift (ppm)			
	LiBF_4		$(\text{C}_2\text{H}_5)_4\text{NBF}_4$	
	No C6P	With C6P	No C6P	With C6P
$\text{CH}_2\text{Cl}_2/\text{ACN}$ 1:9	-150.08	-149.99	-149.90	-149.91
$\text{CH}_2\text{Cl}_2/\text{ACN}$ 5:5	-153.23	-152.83	-151.55	-151.56
$\text{CH}_2\text{Cl}_2/\text{ACN}$ 9:1	-148.89	-150.66	-151.67	-151.69

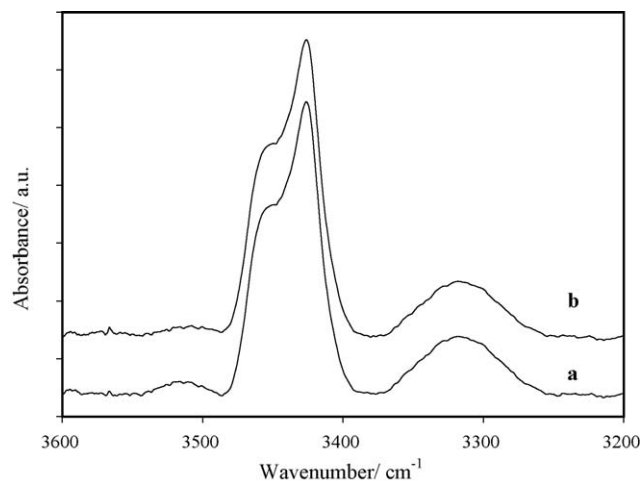


Fig. 3. FTIR spectra of C6P/glyme solution (a) and C6P/glyme/LiTf solution, C6P:salt molar ratio 1:3 (b). C6P content was equal to 20 mmol/kg.

tive can be found at lower salt concentrations (0.5–0.75 mol/kg) rather than in samples without additives (1.0 mol/kg). This can suggest that the decrease in conductivity is associated with complexation of an anion and higher negative charged associates transport suppression in samples with supramolecular additive.

The change of the additive content seems to have a negligible effect on conductivity.

3.4. Lithium transference numbers measurements

The transference numbers of t_{Li^+} obtained are shown in Fig. 5. As one can easily notice, they are generally higher in samples with supramolecular additive. This is in agreement with results reported by us in the case of PEODME-LiBF₄-C6P system [30]. This is especially true for samples with the highest conductivity. It seems that the main problem is the instability of the lithium–electrolyte interface in the presence of even a small electric field.

The growth of passivation layer and change in overall resistance of sample connected with this effect is not the only phe-

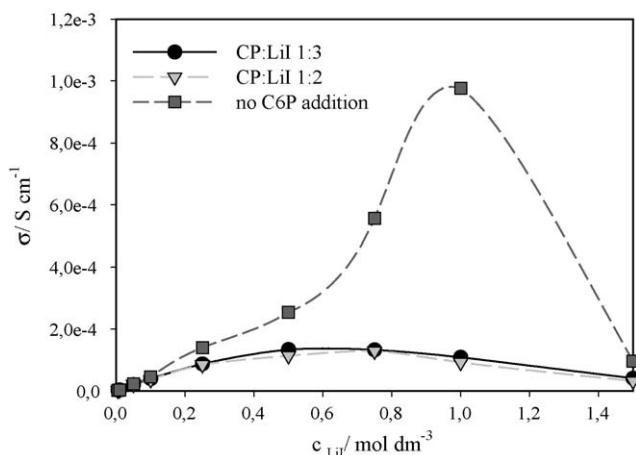


Fig. 4. Conductivity of PEODME-LiI-C6P systems.

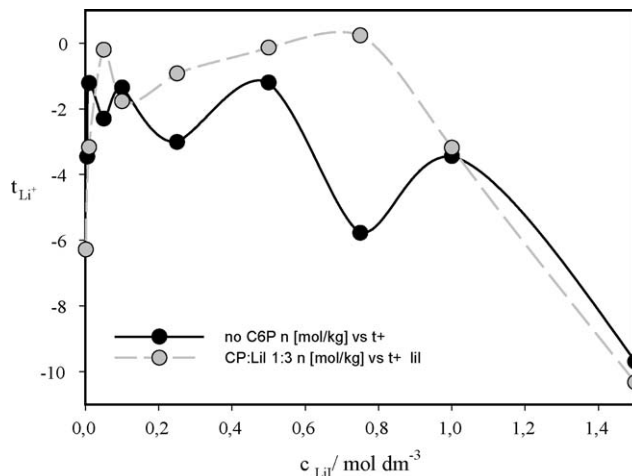


Fig. 5. Li⁺ cation transference numbers in PEO-LiI-C6P system (LiI:C6P = 3:1).

nomenon we face. The formation of the passivation layer is partially an electrochemical reaction and, thus, decreases the current efficiency of main process (lithium transport). Additionally, the charge carrier transport mechanisms within the layer are different in comparison with the bulk electrolyte. Finally, we can assume that the measured value is an average of the electrolyte and layer properties which change with the passivation layer growth.

Negative values of t_{Li^+} can be explained by the assumption of significant contribution of charged aggregates, e.g. LiI₂⁻ triplets to ionic transport. In the case of this kind of the charged species, the mass transport of lithium is connected with electric transport of the negative charge. Thus, the contribution of the negative charged triplet to the lithium transference number is equal to -1.

3.5. Conductivity of GELS

Gels prepared with the use of both methods exhibited similar values of ionic conductivity, with an Arrhenius type temperature dependence activation energy of conduction equalled to 10–20 kJ/mol, typical for liquid organic electrolytes. The addition of C6P did not affect the conduction parameters significantly. The graph (Fig. 6) presents conductivity changes for two-step synthesis gel containing LiCF₃SO₃.

3.6. Impedance of Li-GEL interface

The impedance spectra matched the overall equivalent circuit of serial connection of parallel resonators corresponding to conduction phenomena (HF), interfacial layer (MF) and charge transfer (LF), as shown in idealized impedance spectra depicted in Fig. 7.

Examples of Nyquist graphs typical for our experiments are presented in Fig. 7. A significant growth of overall impedance is observed for all Li cells. Numerical fit of these spectra to the equivalent circuits indicates that two phenomena are affected by the C6P addition. Changes of resistances of corresponding sub-circuits are shown in Fig. 8. The passive layer resis-

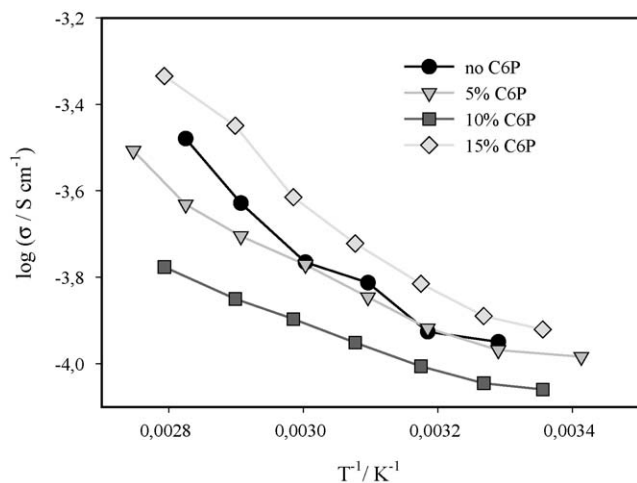


Fig. 6. Conductivity of PVdF gels (PC-LiCF₃SO₃-C6P).

tance R_{MF} is significantly lower during the prolonged test (up to 240 h) in 5% and 10% gels containing C6P. The values of charge transfer resistance R_{LF} show a tendency to grow after a longer time of Li exposure to the gel. All impedance results are very irregular, especially for 10% C6P containing gels. The reason might be a structural difference between two sides of a gel separator, as projected by scanning electron microscope analysis. The additive is not completely dissolved in the electrolyte and tends to sedimentate during the 3–4 h of curing and hardening of the gel. It is, however, possible that in suspensions complexes can be formed on the surface of C6P grains.

3.7. C6P electrochemical behaviour

In the presence of C6P an anodic peak appeared at ca. 0.7 V/NHE in the gel electrolyte (Fig. 9). Further CV-grams were registered in PC solutions (Figs. 10 and 11). The peak, as shown in Fig. 10, forms only in solutions of lithium salts with anion complexed by C6P macrocyclic ring—LiBF₄ and LiCF₃SO₃.

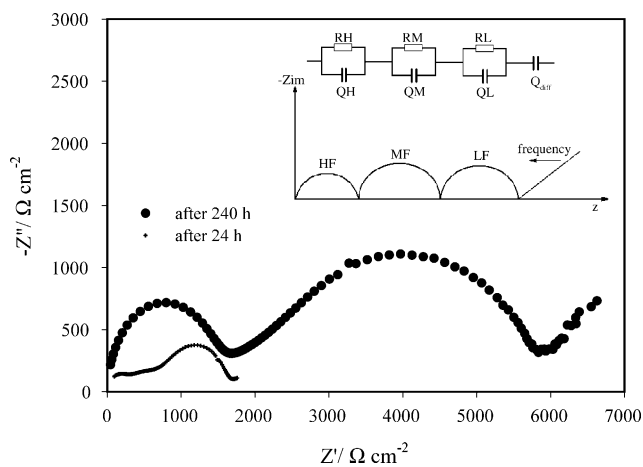


Fig. 7. Nyquist plots of Li/gel/Li cell with 5% C6P in the electrolyte. Frequency range 0.1 Hz–1 MHz. Equivalent circuit used in fitting procedure given in the right corner.

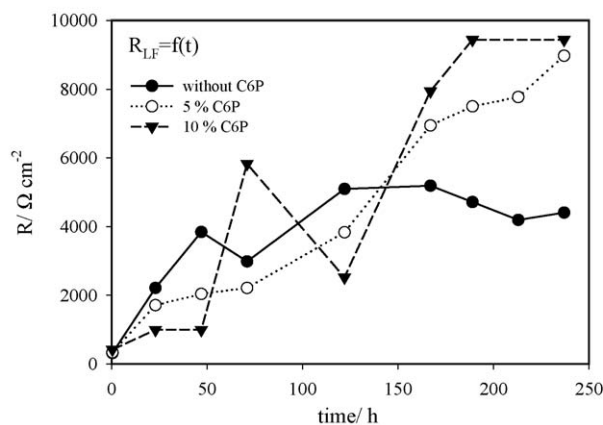
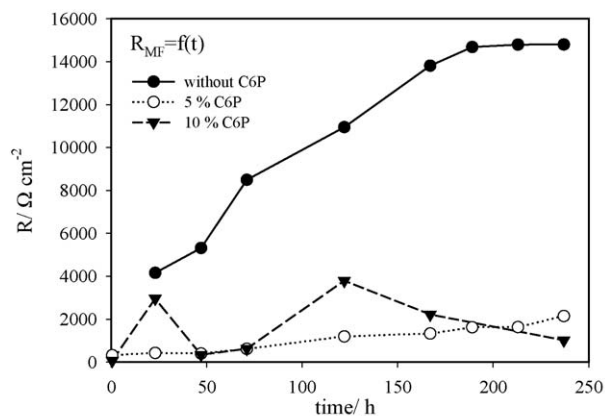


Fig. 8. Changes of the passive layer (R_{MF}) and charge transfer (R_{LF}) resistances in time.

Sodium salts, such as NaBF₄, as well as Et₄NBF₄ and LiClO₄ do not exhibit anodic waves at these potentials. More concentrated solutions could not be studied, because of poor solubility of C6P in PC and other polar solvents.

The anodic peaks tend to disappear with time (Fig. 11), suggesting that the equilibrium state of the complex formation is reached slowly and does not exhibit any further electrochemical activity.

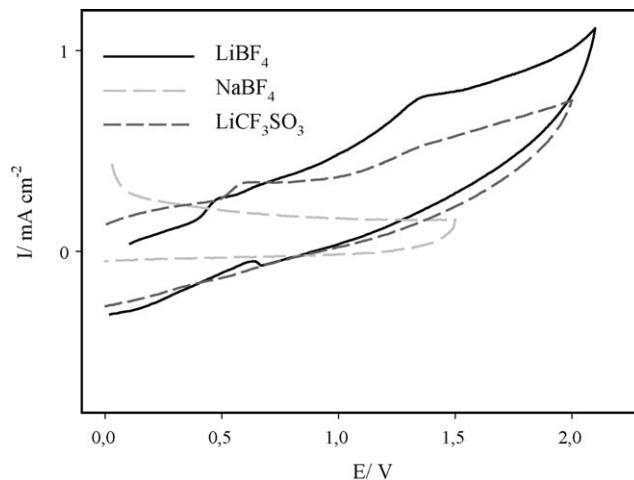


Fig. 9. Comparison of CV characteristics of PVdF/PC gel electrolytes, scan rate 50 mV s⁻¹, potential given vs. NHE.

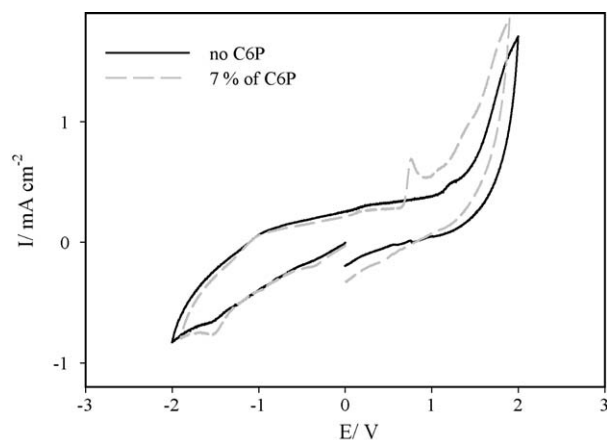


Fig. 10. Anodic activity in PC solutions of different salts. Scan rate 50 mV s^{-1} , potential given vs. NHE.

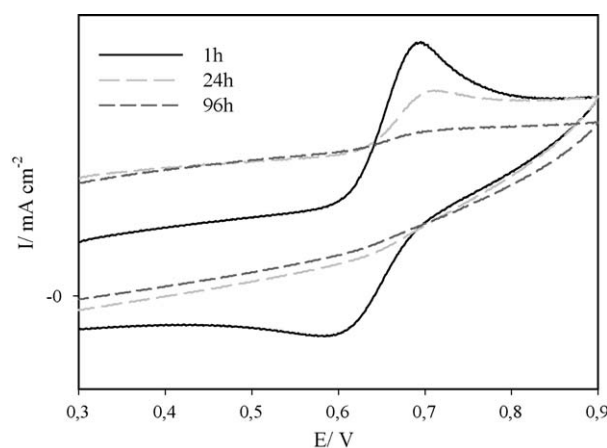


Fig. 11. Anodic oxidation peak dependence on time in Li-triflate/PC solution. Scan rate 50 mV s^{-1} , potential given vs. NHE.

4. Conclusions

In $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ mixtures, studies of the ^{19}F NMR chemical shift change show clearly that complexation of anions takes place. The complexation equilibrium is affected by the increasing dielectric constant of the solvent. Independently of the fact that the receptor is anion sensitive, the complexation equilibrium is also affected by the cation type. This phenomenon can be attributed to the changing ion association equilibrium with the cation change. These results are in agreement with improvement of t_{Li^+} in PEO- $\text{LiBF}_4\text{-C6P}$ and PEODME- $\text{LiBF}_4\text{-C6P}$ systems, studied by us previously.

In liquid systems as PEODME- LiI-C6P and published by us previously PEODME- $\text{LiBF}_4\text{-C6P}$, the overall conductivity is decreased by the addition of C6P. Contrary to the solid electrolytes, the anion trapping effect (lowering the conductivity and increasing the t_{Li^+}) is stronger in comparison to the cation liberation.

Instability of the lithium electrode-PEODME-based (liquid) electrolyte interface affects transference number measurements, causing their incoherence. It is in opposition to the lithium electrode-PEO-based (solid) electrolyte interface. Gen-

erally, addition of C6P leads to the increase of transference numbers.

However, low solubility of C6P in polar solvents makes further electroanalytical studies impossible, the complexes of C6P with lithium salts exhibit some electrochemical activity—anodic waves are observed in PC solutions of lithium salt of complex-forming anions. Synthesis of polar anion receptors could contribute to an explanation of the observed phenomena.

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