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Lithium ion transport of solid electrolytes based on PEO/CF_3SO_3Li and aluminum carboxylate

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Abstract

A homogeneous, composite polymer electrolyte (PE) containing poly(ethylene oxide) (PEO), CF_3SO_3Li and 33 wt.% of aluminum carboxylate $[RC(O)OAlEt_2]_2$ with an oligooxyethylene group $R = CH_2CH_2C(O)O(CH_2CH_2O)_nCH_3$ ($n = 7$) (AlCarb7), characterized by low glass transition temperature $T_g = -51.4\,°C$ was prepared. The interaction of aluminum carboxylate with various lithium salts was characterized on the basis of ^{27}Al NMR spectroscopy in $CDCl_3$ solutions. The bulk conductivity of solid PE with AlCarb7 is of the order of $10^{-5}\,S\,cm^{-1}$ at 60 °C and $10^{-4}\,S\,cm^{-1}$ at 90 °C. Electrochemical tests of Li|PE|Li cells showed a decrease in the R_{SEI} with temperature, stabilizing at about $10\,\Omega\,cm^{-2}$. The lithium ion transference numbers determined by ac–dc polarization experiments range from 0.7 to 0.9. ^7Li, ^{19}F and ^1H NMR spectra, the relaxation time and diffusion data were obtained. The calculated lithium transference number t_+ at 50 °C is equal to 0.995, which suggests practically complete immobilization of the triflate salt anions. In the range of high temperatures (130–180 °C) t_+ is equal 0.35–0.39. The dependence of t_+ on temperature should probably be connected with the partial dissociation of the aluminum carboxylate and lithium salt complex.
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Keywords: Lithium polymer electrolytes; Aluminum carboxylates; Lithium transference number; Lewis acid additives

1. Introduction

Numerous works on the possibility of utilizing plastic, light solid polymer electrolytes (SPE) as separators in lithium rechargeable batteries and other electrochemical devices such as sensors and displays are being carried out [1,2]. However, their industrial utilization is limited by the too low ionic conductivity over the temperature range in which they maintain their good mechanical properties. Systems containing polar organic solvents are characterized by suitably high conductivity, but their volatility and relatively high chemical reactivity cause that new solvent-free materials are continuously searched for.

The hitherto carried out studies on polymeric materials indicate that the poly(ethylene oxide) amorphous phase is characterized by the best ability for ion conduction. Hence a considerable number of works have been devoted to the modification of electrolytes involving PEO to reduce its tendency towards crystallization and increase the ionic conductivity. From the point of view of the operating parameters of a battery, besides appropriate high ionic conductivity it is required for the electric charge to be transported exclusively or mainly with the participation of lithium cations, since only they undergo the reversible electrode reaction. Depending on the measurement method and the salt concentration, the lithium transference number values of SPE based on PEO lie in the 0–0.5 range [3]. The obtainment of an electrolyte of the lithium cationic transference number equal or close to unity is one of the conditions of technology development involving SPE. The cation transference number equal unity is characterized by polyelectrolytes in which the anions are chemically bonded with the polymer matrix, but their conductivity in the absence of a polar solvent facilitating the dissociation of ions is very low [2,4]. There are many works in the literature concerning the achieving of the effect of partial anion immobi-

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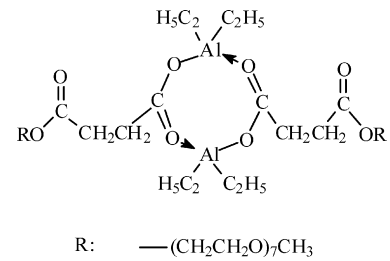
lization in SPE. The synthesis of composite systems involving nanosized inorganic particles like γ-$LiAlO_2$, TiO_2 or Al_2O_3 embedded in the host matrix is one of the intensively developing topics of studies concerning SPE modification. It was suggested that the addition of some inorganic materials leads to an increase in the lithium transference number and also the conductivity of electrolytes and stability of the layer on the lithium electrode/electrolyte interface [5–9]. The other method consists in the introduction of so called receptors of anions causing a decrease in the share of ion pairs and immobilization of anions, resulting in an increase in the cation transference number. The role of anion receptors can be fulfilled by supramolecular compounds such as calixarenes [10,11] or calixpyrroles [12], or by compounds of a Lewis acids character capable of complexing salt anions, in the form of organic boron [13–16] or aluminum derivatives [17]. Active centers of an acidic character may also be incorporated into the polymer matrix of a linear structure [18,19], or by the polycondensation reaction with the formation of a cross-linked structure [20].

The subject of the present paper are electrolytes based on PEO complexes with lithium salts comprising an organic aluminum derivative in the form of a dialkylcarboxylate $[RC(O)OAlEt_2]_2$ containing oligooxythylene groups $R = CH_2CH_2C(O)O(CH_2CH_2O)_nCH_3$ ($n = 7$). From our earlier works it appears that both alkoxy and carboxylic derivatives of aluminum favorably affect the mechanical properties of the membranes, also at elevated temperature, and cause an increase in ionic conductivity [21,22]. In this work we present the results of studies carried out to explain the mode of interaction of the organoaluminum derivative with the other components of the electrolyte. To show the interactions of aluminum atoms in the carboxylate with the lithium salt anions, ^{27}Al NMR studies of solutions in a non-donor solvent ($CDCl_3$) were performed. The limitation of the anionic conductivity, and thus increase in the lithium cation transference number, is an expected result of interaction of the aluminum compound of Lewis acid properties with the basic salt anion. The lithium transference number of the electrolytes studied by us containing PEO, $LiCF_3SO_3$ and aluminum carboxylate was determined by two methods, by an electrochemical method involving the steady-state technique and by self-diffusion measurements by means of PGSE NMR. In this work the effect of temperature on the formation of aluminum carboxylate complexes with the lithium salt and on the electrolyte transport properties involving this salt have been studied.

2. Experimental

2.1. Synthesis of diethylaluminum carboxylate (AlCarb7)

Diethylaluminum carboxylate (AlCarb7) was obtained in a two-step reaction as described earlier [22]. In the first step diethylaluminum oligo(oxyethylene) alkoxide was obtained in the reaction of triethylaluminum and oligo(oxyethylene glycol) monomethylether of $M_w = 350\,g\,mol^{-1}$. The obtained diethylalkoxyaluminum compound was then subjected to reaction with succinic anhydride at toluene boiling point for 20 h. Examples of the reaction of aluminum alkoxides with carboxylic acids as well as acid anhydrides may be found in the literature [23]. The cryoscopic determinations carried out by us show that this compound occurs mainly in a dimeric form.



2.2. Preparation of polymer electrolytes

The electrolytes were obtained according to the standard procedure by film casting of poly(ethylene oxide) (PEO) ($M_w = 5 \times 10^6\,g\,mol^{-1}$), aluminum carboxylate (AlCarb7) and CF_3SO_3Li from a mutual solution in acetonitrile. The following electrolyte composition was applied: 67 wt.% of PEO, 33 wt.% of AlCarb7 in the presence of lithium salt, 10 mol% with respect to ethylene oxide monomeric units present in PEO and oxyethylene substituents in aluminum carboxylate. The mixed components formed a homogeneous solution. All operations connected with the obtaining of electrolytes and performing the measurements were carried out in an atmosphere of dried argon. The solvent was removed under dynamic vacuum in two steps, first for 50 h at a vacuum of 20 Torr and then for 140 h at 10^{-3} Torr at room temperature. In the FTIR spectrum, the signals assigned to acetonitrile completely disappeared after about the first 70 h of such drying. The solvents were dried and distilled in an argon atmosphere prior to use. $LiCF_3SO_3$ (Aldrich, reagent grade) was dried at 120 °C under a vacuum of 10^{-4} Torr for 24 h. The electrolytes thus obtained form flexible and homogeneous membranes. The final thickness of the film was about 350 μm.

2.3. Electrochemical measurements

For the determination of electrochemical properties of the polymer electrolyte (PE) symmetrical Li|PE|Li hermetically sealed 2032 coin cells were assembled and tested with the use of a computer-interfaced Solartron 1260 frequency-response analyzer over the frequency range: 1 MHz to 0.1 Hz. The area of the polymer electrolyte sample was 1.8 cm^2 and that of Li electrodes: 0.96 cm^2. The distance between the lithium electrodes is actually equal to the thickness of the solid polymer electrolyte film. The test temperature range varied from 25 to 110 °C.

The lithium ion transference number (t_+) of polymer electrolytes was determined by a well established steady-state technique introduced by Bruce et al. [24] and Appetecchi et al. [25]. The method is based on the analysis of combined dc and ac runs on the symmetrical cell with non-blocking lithium electrodes. The dc measurements of initial (I_0) and the steady-state (I_{ss}) currents were made by polarizing the test cells at

voltage bias of 10 mV. The ac impedance measurements were performed before and after applying a bias, to evaluate the value of the interfacial resistance at the beginning and at the end of the test, *i.e.*, R_0 and R_{ss}, respectively. Under these conditions, the lithium ion transference number is given by the equation:

$$t_{Li+} = \frac{I_{SS}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{SS} R_{SS})} \quad (1)$$

The lithium ion transference number of the membrane samples was measured between 60 and 105 °C.

2.4. Solid state ^{1}H, ^{7}Li and ^{19}F NMR measurements

The NMR measurements were made on a Chemagnetics CMX-300 spectrometer used in conjunction with Japan Magnet Technology 7.1 T superconducting magnet. In this field the ^{1}H ($I = 1/2$), ^{7}Li ($I = 3/2$) and ^{19}F ($I = 1/2$) resonances occur at $\omega_0/2\pi = 301.0$, 117.0 and 283.2 MHz, respectively. Spectra and transverse and longitudinal relaxation times were measured (T_2, T_1). The pulse gradient spin echo (PGSE) NMR measurements were performed using a 5 mm dual broad band gradient DOTY and DIFF60 probes. Experimental details are described elsewhere [26].

The Hahn spin-echo pulse sequence [27] and the stimulated echo sequence [28], which is useful for situations when $T_2 < T_1$, were used to measure the self-diffusion coefficient. The echo amplitude is attenuated by an amount dependent on how much the position of the spins has changed by process of self-diffusion in the time interval Δ. It can be shown that the attenuation of the spin-echo amplitude is given by the Stejskal–Tanner equation:

$$A(g) = \exp\left[-(\gamma g \partial)^2 D \left(\Delta - \frac{\partial}{3}\right)\right] \quad (2)$$

where D is the self-diffusion coefficient and γ is the magnetogyric ratio of the spin. The diffusion coefficient D is determined by fitting this equation to the echo amplitudes for a series of gradient strengths g (0.2–18 T m^{-1}). Typical reproducibility of the diffusion coefficient measurements is about ±3%. Thin films of the electrolyte were sealed under argon in 5 mm NMR tubes. The samples were equilibrated for at least 30 min. An Oxford ITC533 temperature accessory in conjunction with a stream of dry N_2 gas was used to regulate the temperature to within ±1 K.

2.5. ^{27}Al NMR studies

^{27}Al NMR spectra were recorded on a Varian Mercury 400 spectrometer in $CDCl_3$ and DMSO-d_6 solutions at 25 °C.

2.6. DSC studies

The DSC studies were carried out on a Perkin-Elmer (Pyris) apparatus in the −100 to 200 °C temperature range with a heating rate of 20 °C min^{-1} in hermetically closed aluminum vessels.

2.7. SEM

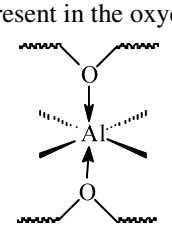
A JSM 6300 scanning microscope (Jeol Co.) equipped with a Link elemental analyzer and a silicon detector was used for the study of surface morphology.

3. Results and discussions

3.1. ^{27}Al NMR studies of aluminum carboxylate

Aluminum carboxylate containing seven monomeric units of EO in the ester group (AlCarb7) is an amorphous compound of $T_g \sim -60.5$ °C. From our earlier observations it appears that this temperature clearly increases after introducing the lithium salt, which may indicate the formation of complexes between the EO monomeric units and Li^+ cations [22]. At the lithium salt content of 10 mol% with respect to the EO monomeric units the T_g value for AlCarb7 and CF_3SO_3Li mixture is −32 °C. The interaction of the lithium salt with aluminum carboxylate may be also observed in ^{27}Al NMR spectra. In Fig. 1 are presented the ^{27}Al NMR spectra of AlCarb7 and its mixtures with various lithium salts in the form of $CDCl_3$ solutions.

As can be noticed in Fig. 1, the signal of aluminum in AlCarb7 occurs in the region characteristic of six-coordinative aluminum, and its chemical shift depends on the type of solvent; in DMSO it is 10.08 ppm, and in $CDCl_3$ it is equal to 7.11 ppm. We assume that aluminum atoms in the carboxylate undergo coordination by the oxygen atoms present in the oxyethylene substituents.



As a result of interaction with aluminum carboxylate, some of the lithium salts studied by us, such as $LiClO_4$, CF_3SO_3Li, $(CF_3SO_2)_2NLi$ and CH_3COOLi gain solubility in chloroform, while for salts containing small, hard anions such as LiF and LiCl this interaction is weak and the solubility of these salts in chloroform in the presence of AlCarb7 is small. In ^{27}Al NMR spectra of AlCarb7 and lithium salts solutions the aluminum signal still is present in the region characteristic of the full saturation of the coordination sphere, but undergoes a shift by *ca.* 15 ppm towards negative values. This shift depends on the strength of interaction of the salt anions and aluminum. In the case of $LiClO_4$ the chemical shift of aluminum is −9.44 ppm, which probably indicates the strongest interaction of the anion of this salt with aluminum. For the imide salt the signal shift is −8.41 ppm, and a similar chemical shift is observed for the lithium triflate −8.25 ppm.

For the AlCarb7 and lithium acetate solution signals are present in the spectrum characteristic of both the form complexed by the salt anion of the shift of −7.72 ppm, as well as of the initial form of chemical shift of 7.08 ppm. There is still one signal of the chemical shift of 3.54 ppm present in this spectrum. In order to determine the origin of this signal,

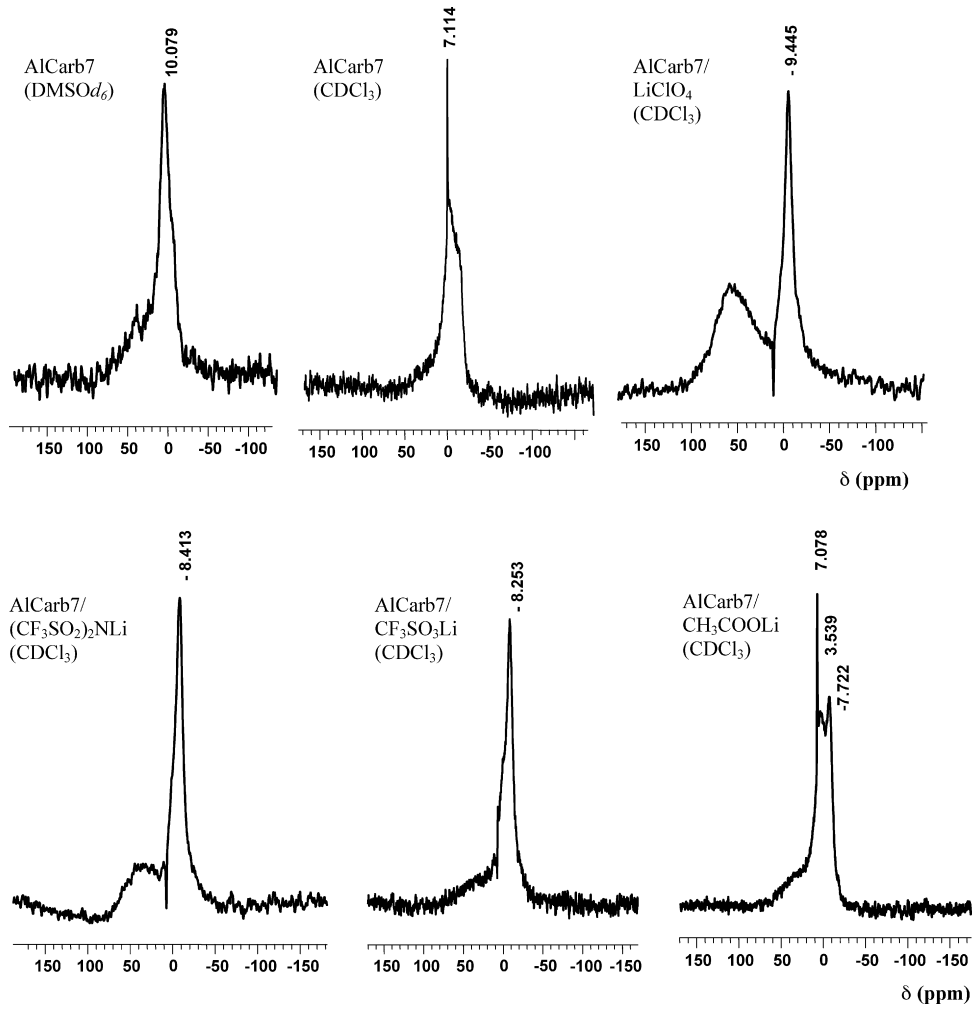


Fig. 1. ^{27}Al NMR spectra of AlCarb7 (in $CDCl_3$ and DMSO-d_6) and solutions of AlCarb7 with equimolar ratio of different lithium salts (in $CDCl_3$).

a spectrum of AlCarb7 solution with a two-fold molar share of CH_3COOLi salt was recorded. This spectrum is presented in Fig. 2. We observe in it also three signals, but their mutual intensity changed. The signal at 4.03 ppm is the most intense one, indicating the possibility of aluminum complexation by two salt anions. Moreover, uncomplexed AlCarb7 in low concentration, as well as the complex with the participation of one anion, are present. The spectra presented show a greater facility of the aluminum salt formation involving two carboxylate anions, with respect to the other salts studied.

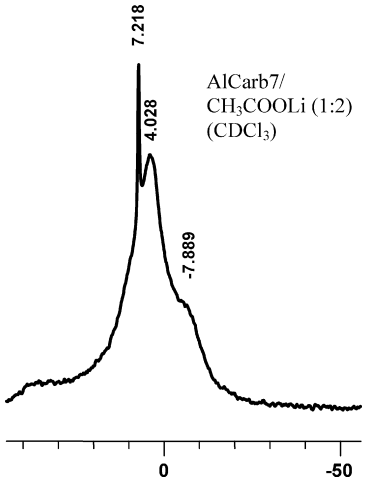
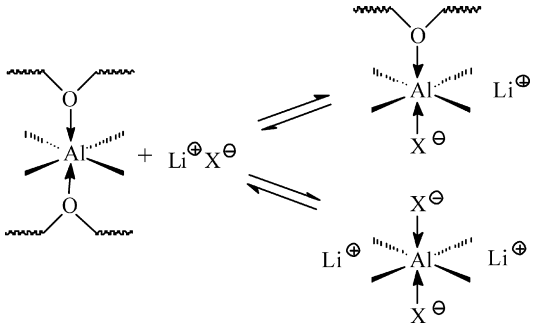


Fig. 2. ^{27}Al NMR spectrum of the AlCarb7 mixture with CH_3COOLi at molar ratio 1:2 (in $CDCl_3$).



3.2. Characterization of PEO/AlCarb7/CF_3SO_3Li electrolyte

In Fig. 3 is presented the DSC thermogram of the studied electrolyte PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li, in which the

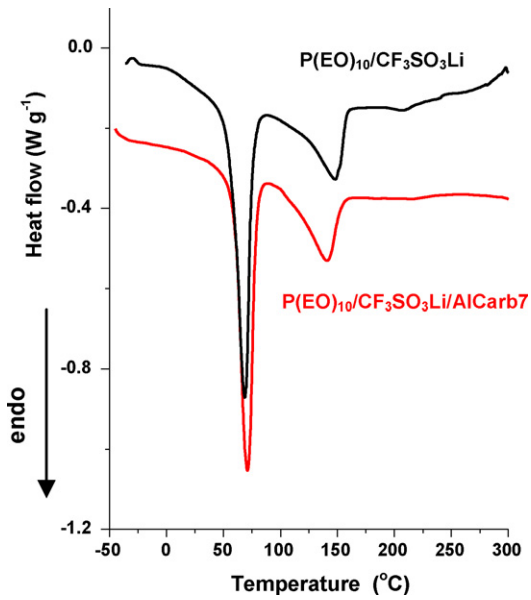


Fig. 3. DSC thermogram of the electrolyte PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li.

share of the salt is 10 mol% with respect to the EO monomeric units and for comparison, of the PEO complex with 10 mol% of CF_3SO_3Li. In the thermogram two endothermic first order transitions, a melting peak of the crystalline PEO phase with a maximum at 70.9 °C and a second broad signal with a maximum at 140 °C connected with the melting of the crystalline complex phase formed between PEO and $LiCF_3SO_3$ [29,30] can be distinguished. The DSC trace of AlCarb7-containing polymer electrolyte is very similar to that of the additive-free PEO film, however, in the presence of the additive the onset point of the second endotherm is shifted by 8 °C towards lower temperatures. In our earlier work [22] we showed that the addition of aluminum carboxylate additives to such systems does not cause a decrease in the ability to crystallize the PEO chains (and in some systems it causes a clear increase of it) during the solvent evaporation. Moreover, this system is characterized by low glass transition temperature (T_g), which takes place at −51.4 °C [22], and hence is by several degrees lower than that of the $P(EO)_{10}$–CF_3SO_3Li system [30].

The surface morphology of the studied electrolyte was characterized by scanning electron microscopy (SEM), and the images obtained are presented in Fig. 4. As can be seen, the polymer electrolyte sample is very homogeneous without clear crystalline domains. At high magnification some irregularities appear as amorphous regions, which are formed during solvent evaporation while drying of the membranes.

3.3. Electrochemical characterization of the PEO/AlCarb7/CF_3SO_3Li electrolyte

AC impedance measurements were carried out in the symmetrical cell with non-blocking lithium electrodes. The complex AC response of Li|solid polymer electrolyte|Li systems is typically fitted to an equivalent circuit (Fig. 5), where C_g is the geometrical capacitance of the cell, R_b the bulk resistance; R_{gb} and C_{gb}, grain boundary resistance and capacitance; R_{SEI} and C_{SEI} are solid electrolyte interphase resistance and capacitance. Fitting of experimental data to an equivalent circuit has two main problems. First, the elements are not ideal and there is always some sort of distribution around the relaxation frequencies and secondly, it is difficult to obtain a good fit when

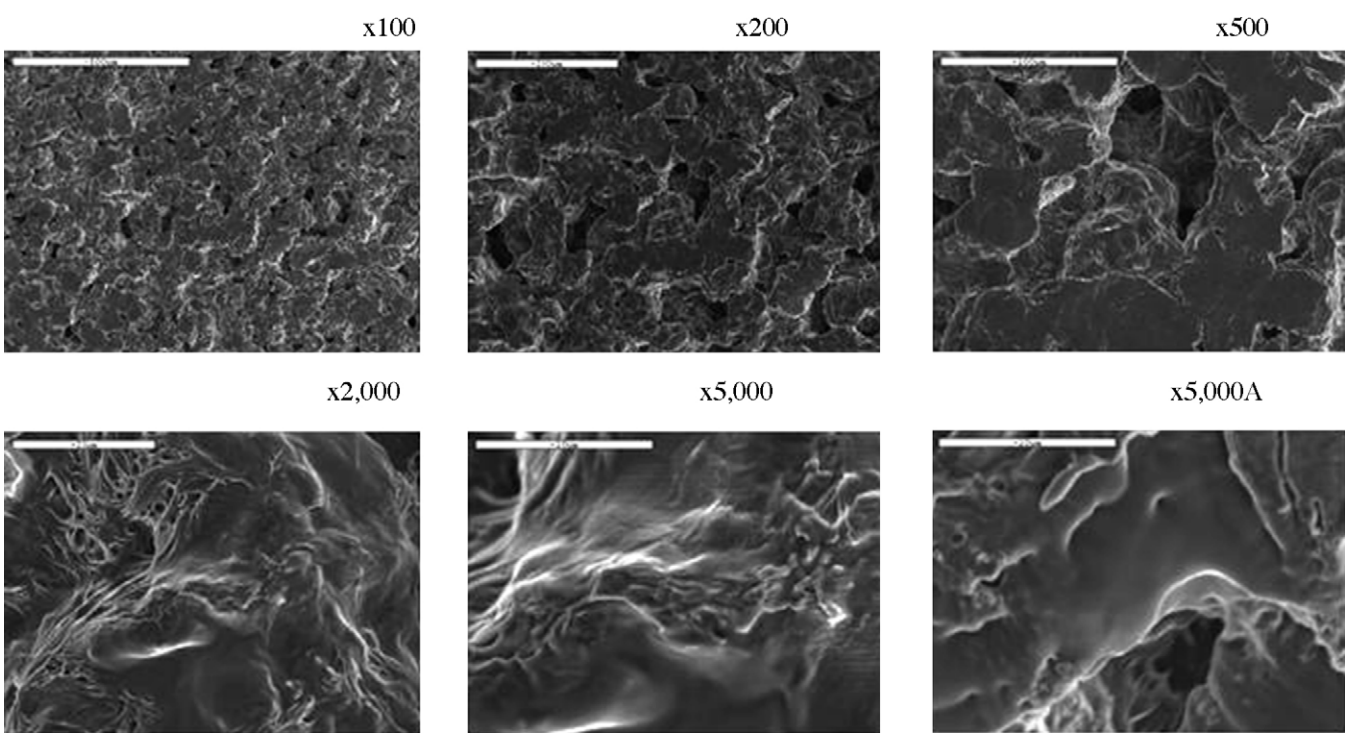


Fig. 4. SEM micrographs of the electrolyte PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li.

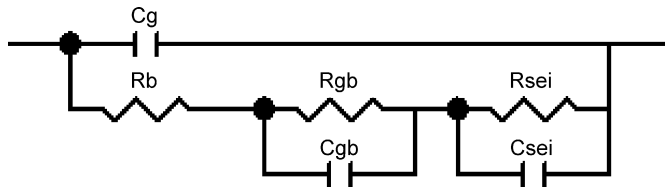


Fig. 5. Equivalent circuit for Li|PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li|Li cell. C_g: geometrical capacity; R_b: bulk resistance; R_{gb} and C_{gb}, grain boundary resistance and capacitance; R_{SEI} and C_{SEI}: solid electrolyte interface resistance and capacitance.

the difference between relaxation frequencies of contributing elements is small, due to the uncertainty in the estimation of the starting parameters. Therefore, different alternative representations have been used to resolve the overlapped processes and to calculate the relative contribution of bulk, gb, and SEI resistance to the total cell impedance. Impedance values were obtained by a non-linear least square fitting of each arc of the complex spectra, when the gb arc was well-pronounced (Fig. 6a). In other cases (Fig. 6b) the circuit parameters were calculated according to the model shown in the Fig. 5. Chi-

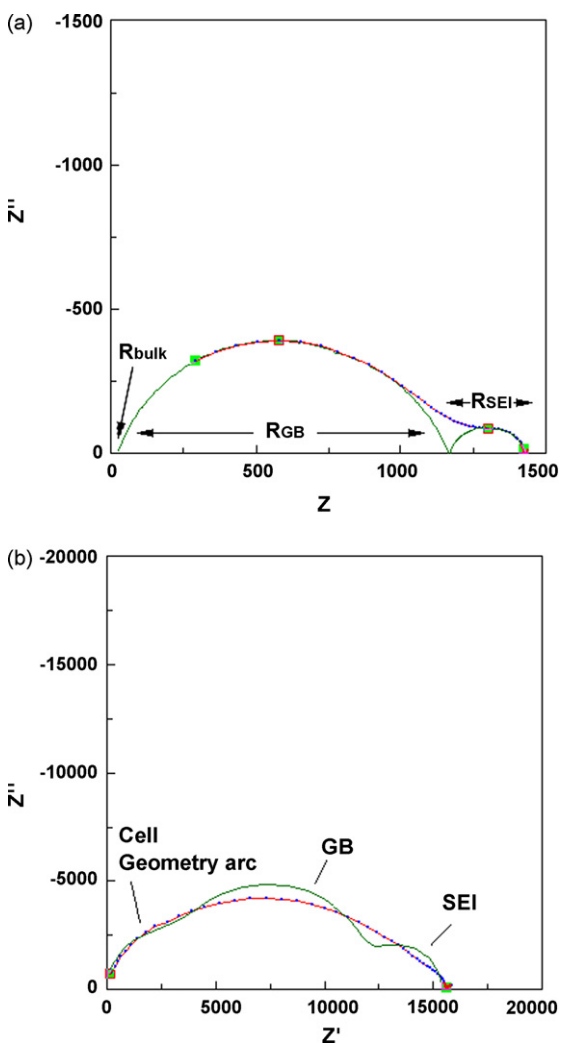


Fig. 6. Nyquist plots of the Li|PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li|Li cell at 60 °C (a) and 55 °C (b).

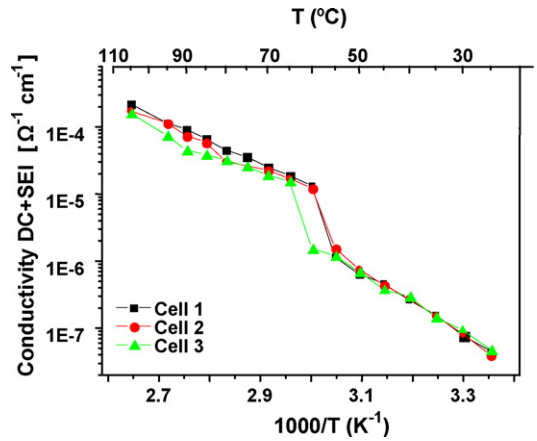


Fig. 7. Arrhenius plots of the Li|PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li|Li cells — total conductivity data.

squared distribution value (χ^2) was about 0.03. Fig. 6a shows an exemplary Nyquist plot obtained at about 60 °C, for the studied PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li electrolyte, where two clear semicircles have been distinguished. The capacitance of the first high-frequency arc was about 0.75 nF with the frequency maximum 50 kHz. The capacitance of the second arc at f_{max} of 1.3 kHz is 0.6 nF. The calculated geometrical capacity of the cell is 45 pF, suggesting that the permittivity of the polymer electrolyte is about 10. Therefore, the first semicircle was attributed to the grain-boundary resistance and the second to the resistance of solid electrolyte interface, formed on Li electrodes.

Three identical Li|PEO/AlCarb7/CF_3SO_3Li|Li cells were tested and the electrochemical data are shown in Figs. 7–9. Fig. 7 represents the conductivity of the three identical Li|polymer electrolyte|Li cells, calculated from the total impedance data including bulk, grain-boundary and SEI resistances. High data reproducibility should be mentioned. The conductivity of the cells gradually increases from 10^{-8} S cm^{-1} at 30 °C to 10^{-4} S cm^{-1} at 90 °C. The course of conductivity changes is characteristic for electrolytes containing PEO as the polymeric matrix, showing a tendency towards crystallization. At *ca.* 60 °C a jump in conductivity by about an order of magnitude occurs,

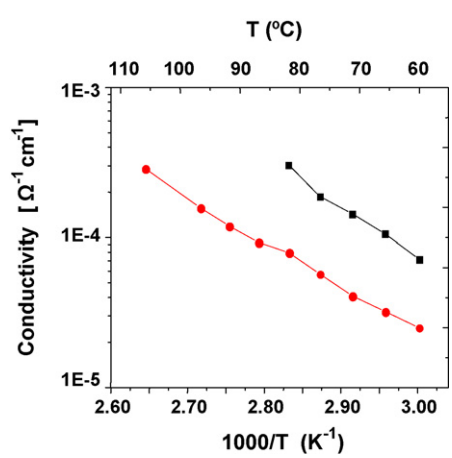


Fig. 8. Bulk (●) and grain boundary (■) conductivity of the Li|PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li|Li cells.

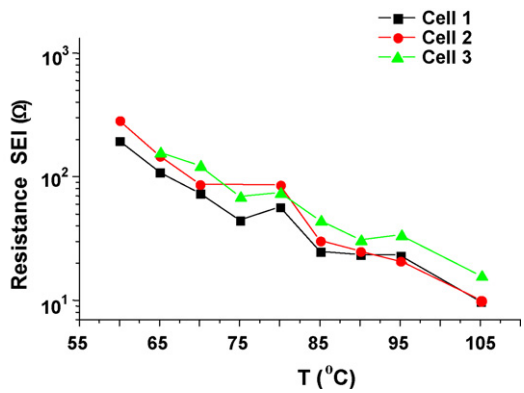


Fig. 9. Resistance of the SEI vs. temperature plots.

connected with the melting of the PEO crystalline phase (Fig. 3). In the temperature range above T_m only the polymer amorphous phase, much more efficient in ion transport, is present.

As can be seen from Fig. 8, the grain-boundary conductivity is more than three times that of the σ_{bulk}. At above 80 °C the GB arc vanishes. In addition, it should be mentioned, that the σ_{bulk} absolute values of the PEO/AlCarb7/CF_3SO_3Li polymer electrolyte are relatively high and reach 10^{-4} S cm^{-1} at above 90 °C.

In Fig. 9 are presented the changes in resistance of the SEI as a function of temperature. The initial R_{SEI} value is high, at 60 °C it is 200–300 Ω. With a rise of temperature the resistance of the SEI decreases and at above 100 °C the R_{SEI} is lower than 10 Ω cm^2.

The values of the lithium ion transference number of the polymer electrolyte determined by ac–dc polarization experiments are presented in Fig. 10. The transference number of the electrolyte under investigation varies from 0.7 to 0.9. As can be noticed, lower t_+ values were obtained for higher temperature, which probably results from partial dissociation of the aluminum carboxylate complex with the salt with a rise of temperature. Such high t_+ values show a considerable immobilization of the salt anions, which at relatively high ionic conductivity, σ at 60 °C is 6×10^{-5} S cm^{-1}, indicates high mobility of lithium cations in the polymer matrix.

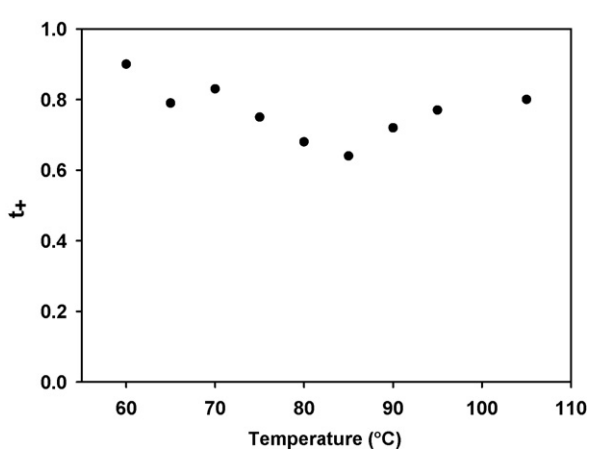


Fig. 10. Plot of transference number vs. temperature of the PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li electrolyte.

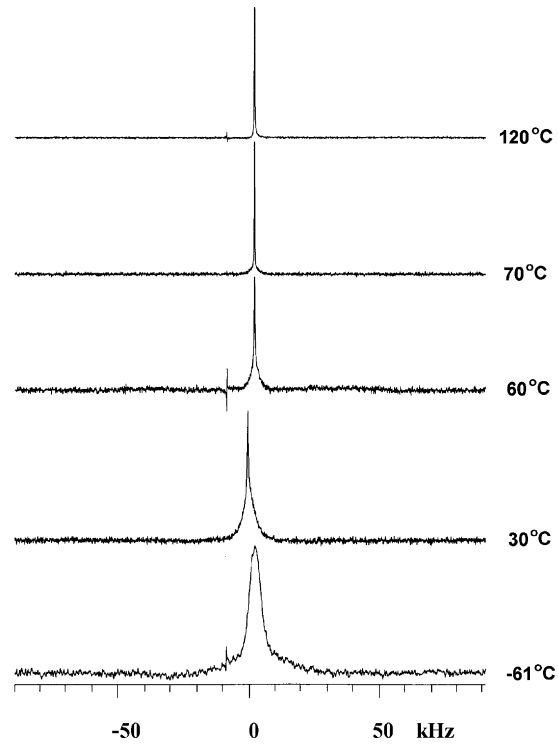


Fig. 11. ^{7}Li NMR spectra of electrolyte PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li as a function of temperature.

3.4. PGSE NMR characterization of the PEO/AlCarb7/CF_3SO_3Li electrolyte

For ^{7}Li, ^{19}F and ^{1}H NMR spectra of the PEO/AlCarb7/CF_3SO_3Li electrolyte, the relaxation time and diffusion data were obtained. The room temperature ^{1}H spectrum exhibits a single lineshape while the ^{19}F spectra consists of a relatively narrow line superimposed on a dominant broader line. The narrow component suggests a small population of highly mobile anions while the broad component may reflect a rigidly bonded configuration of anions. Fig. 11 shows the ^{7}Li spectra as a function of temperature. As is typically observed for polymer electrolyte systems, the ^{7}Li spectra exhibit a broad and a narrow component at temperatures below 60 °C. The broad component is attributed to the $\pm 1/2 \leftrightarrow \pm 3/2$ satellite transitions [31].

Self-diffusion measurements were made at 50 °C and at elevated temperatures greater than 130 °C. The attenuation profile of the signals at 50 °C are shown in Fig. 12 with the solid lines representing the non-linear least square fit of the data. In each case the attenuation profiles could be represented well by a single exponential.

In Table 1 are presented the self-diffusion coefficients D and the lithium transference number t_+ of the PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li electrolyte as a function of temperature. A rough estimate of the lithium transference numbers may be obtained from the expression:

$$t_+ = \frac{D_{Li^+}}{D_{Li^+} + D_{CF_3SO_3^-}} \quad (3)$$

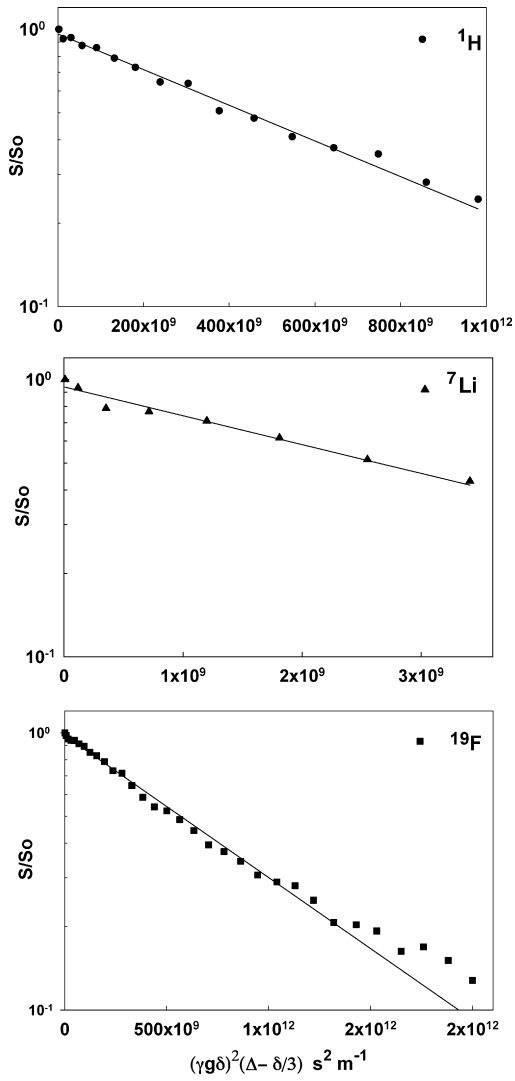


Fig. 12. Signal attenuation of ^{1}H, ^{7}Li and ^{19}F NMR spin-echo spectra as a function of $(\gamma g\delta)^2(\Delta-\delta/3)$ at 50 °C of electrolyte PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li.

As can be noticed, the self-diffusion coefficients strongly depend on temperature. Two temperature ranges can be distinguished, one above 130 °C, for which the lithium diffusion and anion diffusion values are of the order of 10^{-7} cm^2 s^{-1} and the anion diffusion is about twice as high as the lithium cation diffusion.

At a lower temperature of 50 °C, the diffusion of lithium (2.4×10^{-6} cm^2 s^{-1}) is 200 times higher than that for anions (1.2×10^{-8} cm^2 s^{-1}). At the same temperature, the proton diffusion is 1.5×10^{-8} cm^2 s^{-1}, which may indicate that the polymer is strongly coupled with the anion diffusion.

The calculated lithium transference number t_+ at this temperature is very high, it is equal to 0.995, which suggests practically complete immobilization of the triflate salt anions. In the range of high temperatures the lithium transference number is equal 0.35–0.39, with a slight tendency of increase with a rise of temperature. An agreement of these data with the results of t_+ measurements determined by ac–dc polarization experiments, in which t_+ reaches the highest value, equal to 0.9, at 60 °C, occurs. The dependence of t_+ on temperature should probably be connected with the stability of the aluminum carboxylate and lithium salt anion complex. This complex undergoes dissociation at elevated temperature liberating the earlier coordinated salt anions.

4. Conclusions

The studies carried out show that the aluminum carboxylate AlCarb7 used as an additive to the solid polymer electrolyte based on PEO and CF_3SO_3Li salt favorably influences the SPE mechanical and conducting properties. DSC measurements show that the electrolyte involving AlCarb7 is characterized by low glass transition temperature of −51.4 °C. This compound is compatible with the polymeric matrix forming with the lithium salt a homogeneous system, which can be observed in the SEM images.

Electrochemical tests of Li|PE|Li cells with electrolytes involving AlCarb7 showed a decrease of the R_{SEI} with temperature, stabilizing at about 10 Ω cm^2. The conductivity achieved is relatively high, σ_{bulk}, of the order of 10^{-5} S cm^{-1} at 60 °C and 10^{-4} S cm^{-1} at 90 °C.

The electrochemical measurements as well as the NMR diffusion data show that at temperatures below 130 °C the charge transport in these electrolytes proceeds mainly with the participation of lithium cations. At 50 °C the lithium cation transference number is close to unity, which means that $LiCF_3SO_3$/PEO/AlCarb7 electrolyte acts as a solid single ion conductor.

On the basis of an analysis of ^{27}Al NMR spectra of the obtained AlCarb7 compound and its mixtures with different lithium salts it is suggested that the lithium salt anions interact with the carboxylate aluminum atom forming a complex. This interaction results in an increase in the degree of dissociation of the salt. In the presence of AlCarb7 some of the salts studied, such as $LiClO_4$, CF_3SO_3Li, $(CF_3SO_2)_2NLi$ and CH_3COOLi become soluble in chloroform. Due to complexation, the anion

Table 1
Self-diffusion coefficients D and the lithium transference number t_+ for the mobile species of PEO/AlCarb7 (33 wt.%)/CF_3SO_3Li electrolyte as function of temperature

Temperature (°C)	D_{Li^+} ($\times 10^{-7}$ cm^2 s^{-1})	$D_{CF_3SO_3^-}$ ($\times 10^{-7}$ cm^2 s^{-1})	$D_{polymer}$ ($\times 10^{-7}$ cm^2 s^{-1})	t_+
50	24.00	0.12	0.15	0.995
135	2.32	4.28		0.35
145	2.82	4.84		0.37
160	3.83	6.23		0.38
180	5.77	9.06		0.39

formed has a strongly delocalized charge, and due to the high molecular weight, AlCarb7 forms mainly a dimeric low mobile structure ($M_w = 1100$). Possible interaction of lithium cations with oxyethylene monomeric units of AlCarb7 may provide additional conduction paths for Li^+.

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