

The effect of type of the inorganic filler and dopant salt concentration on the PEO–LiClO₄ based composite electrolyte–lithium electrode interfacial resistivity

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Abstract

In the present paper the effect of the type of inorganic filler on the composite polymeric electrolyte–lithium electrode interfacial behavior is analyzed. Studies are performed in the wide LiClO₄ concentration range using poly(ethylene oxide)dimethyl ether (PEODME) as an electrolyte matrix. It is demonstrated that both the formation and the growth of the resistive layers at the polymer electrolyte–lithium electrode interface are determined by the salt concentration range and depend also on the type of the filler used. It is demonstrated that for salt concentrations lower than 10^{−3} mol kg^{−1} or higher than 1 mol kg^{−1} addition of filler results in the suppression of the growth of the resistance of the interfacial layer. This effect has been related to an increase in lithium cation transference number observed in these salt concentration ranges in composite electrolytes compared to the pure PEODME–LiClO₄ analogues. The effect of the filler on conductivity, microstructure and thermal characteristic of electrolytes studied is also discussed.

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1. Introduction

Polymer electrolytes are one of the most promising systems for application in lithium or lithium-ion batteries used in portable devices [1,2]. However, to reach the commercialization step properties of currently used polymer ionic conductors are still not good enough. Among the problems to be solved the low ambient and sub-ambient temperature ionic conductivity, low lithium cation transference number and formation of highly resistive layers at polymer electrolyte–lithium electrode interface are the most important [1,2]. Several synthetic strategies were applied to modify structure and properties of polymeric electrolytes in order to overcome the above-mentioned limitations [2]. Among them the use of inorganic fillers seems to be the most efficient [3]. Addition of fillers results in an increase in ionic conductivity of polymeric electrolytes which also exhibit improved thermal and mechanical properties [4]. Scrosati and co-workers demonstrated that upon addition of inorganic fillers a rise in the lithium transference number occurs [5]. The same

group recognized also the positive effect of inorganic additives on the stabilization of polymer electrolyte–lithium electrode interface [1,4,5]. The suppression of formation and growth of the resistance of interfacial layers has been demonstrated. Similar observations were afterwards reported by a number of research teams which used different types of organic and inorganic additives [3,6–11]. Most of the studies were however performed in the limited salt concentration range corresponding to that practically used in lithium batteries.

In our recent paper we have demonstrated an effect of the salt concentration on the formation and growth of interfacial layers on PEODME–LiClO₄–lithium electrode interface [12]. This effect was coupled to changes in the lithium transference numbers as well as formation of ionic associates. It has been found that resistive interfacial layers are formed at high lithium salt concentrations for which both a low value of lithium transference number and high fraction of ionic associates is present in electrolytes.

Since it is well known that addition of fillers affects both lithium transference number and formation of contact ion pairs and higher associates we decided to study also the effect of fillers on polymer electrolyte–lithium electrode interfacial stability. Studies are performed in the wide LiClO₄ concentration

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range (from 10^{-3} to 3 mol kg^{-1}) using low molecular weight poly(ethylene oxide)dimethyl ether as polymer matrix and variety of nano and microsize fillers. At first the conductivity and microstructure of polymer electrolytes was studied. Changes in the ionic conductivity as the function of type of the filler added and lithium perchlorate concentration are analyzed on the basis of impedance spectroscopy experiments. Ion–polymer interactions are analyzed on the basis of FT-IR experiments. IR data are supported by the studies of the polymer chain flexibility performed by DSC technique. In the next step lithium transference number was calculated for some of the studied electrolytes using the Newman's method [13] adapted by us for liquid-like systems [14]. Finally the stability of polymer electrolytes–lithium electrode interface was evaluated by impedance spectroscopy studies performed in the symmetrical lithium cell with the use of all types of electrolyte.

2. Experimental

2.1. Sample preparation

PEODME ($M_w = 500$, Aldrich, dimethyl capped) was filtered and then dried on a vacuum line first at $\sim 60^\circ\text{C}$ for 72 h and then, under vacuum of 10^{-5} Torr, stringently freeze dried using freeze-pump-thaw cycles. While still, under vacuum, the polymer was transferred to an argon filled dry-box (moisture content lower than 2 ppm) where the salt was dissolved into the polymer using a magnetic stirrer. Salt concentration varied from 10^{-3} to 3 mol kg^{-1} of polymer. Samples of the salt concentration from 3 mol kg^{-1} down to 0.5 mol kg^{-1} were prepared by the direct dissolution of salt in a polymer. Samples of the highest salt concentration were heated up to 50°C to facilitate the dissolution process. Samples of lower salt concentration were prepared by the successive dilution of a batch containing electrolyte with $0.5 \text{ mol kg}^{-1} \text{ LiClO}_4$.

LiClO_4 (Aldrich, reagent grade) was dried under vacuum at 120°C prior to the dissolution. The composite electrolytes were obtained by the dispersion of fillers in a PEODME– LiClO_4 solutions. The concentration of fillers in the composite electrolytes was equal to 10 mass%. Al_2O_3 (Degussa reagent grade, grain size 13 nm), SiO_2 (Degussa reagent grade, grain size 7 nm) and TiO_2 (Degussa reagent grade, grain size 21 nm) were dried under vacuum of 10^{-5} Torr at 150°C for over 72 h prior to the addition to polymer–salt mixture. The same procedure was applied to the self-prepared sulfonated $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 systems of the average grain size equal to $\sim 10\text{--}12 \mu\text{m}$. These later fillers were prepared according to the procedure described elsewhere [15]. Important properties of the fillers applied are summarized in Table 1.

2.2. DSC studies

DSC data were obtained between -110 and 150°C using a UNIPAN 605M scanning calorimeter with a low-temperature measuring head and liquid nitrogen cooled heating element. Samples in aluminum pans were stabilized by slow cooling to -110°C and then heated at $10^\circ\text{C min}^{-1}$ to 150°C . An empty

Table 1
Characterization of the fillers used

Type of the filler	Average grain size (nm)	Average surface area ($\text{m}^2 \text{g}^{-1}$)
SiO_2	7	380
Al_2O_3	13	100
TiO_2	21	50
Sulfonated $\gamma\text{-Al}_2\text{O}_3$	$10\text{--}12 \times 10^3$	83
Sulfonated TiO_2	$10\text{--}12 \times 10^3$	57

aluminum pan was used as a reference. The estimated experimental error of the determination of glass transition temperature (T_g) is equal to $\pm 2^\circ\text{C}$.

2.3. Conductivity measurements

Ionic conductivity was determined using the complex impedance method in the temperature range from 20 to 90°C . The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven. The experiments were performed in a constant volume cylindrical cell of the electrode diameter equal to 7.8 mm and fixed electrolytes thickness equal to 1.6 mm . The impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range $1 \text{ Hz--}1 \text{ MHz}$. The reproducibility of impedance spectroscopy results was checked by multiple experiments performed at room temperature. All results obtained for samples of the same composition do not differ by more than 10%.

2.4. AC impedance studies on Li/PEG-LiClO_4 -filler electrolyte/Li cells

For these studies electrolytes were soaked on polypropylene textile separator of the $210 \mu\text{m}$ thickness. All type of electrolytes with and without fillers were used. Prolonged AC impedance measurements (up to 2 months) in the $1 \text{ MHz--}1 \text{ Hz}$ frequency range with AC amplitude = 20 mV , were performed.

2.4.1. Lithium transference numbers determination

The details of the procedure used and description of the experimental set-up were described in our previous paper [14].

The advantage of the method is that it does not require solution to be dilute or ideal. Because of the solution non-ideality in order to describe completely the transport processes it is necessary to have $n(n-1)/2$ concentration-dependent transport properties, where n is the number of independent species in the solution. To describe PEO–DME– LiClO_4 system the three independent species were chosen to be: Li^+ , ClO_4^- and PEO–DME, without regard for microscopic speciation. To determine individual transport properties following measurements are performed: salt diffusion coefficient–restricted diffusion measurement; cation transference number–concentration cell OCV measurements and symmetric cell polarization.

To facilitate concentration cell experiments the special cell was designed by us and described previously [14]. The cell con-

sists of two half-cells made from polyethylene. After completion of an electrode assembly the electrolyte is put on each half-cell which thereafter are merged and the OCV is measured. The polarization cell experiments were performed in the symmetric cell consisting of two lithium electrodes discs (area 0.5 cm^2) with 0.5 mm distance provided by using Teflon[®] o-ring and Teflon[®] spacer of desired thickness.

Salt diffusion coefficient determination is based on the polarization of the symmetrical cell using direct current till concentration cell is generated. Consequently, potential of the return to the equilibrium state is recorded as a time function. If the relationship is linear diffusion coefficient can be determined from dependency of a slope of a straight line and thickness of electrolyte layer.

Cation transference number measurements were performed in two stages. In the first one the potential of a concentration cell $M|\text{PEODME}_x\text{MX}|\text{PEODME}_y\text{MX}|M$, where x is constant and y varies was measured. The plot $U=f(\ln[c])$ is drawn from measurements. If the investigated system is ideal the plot should be linear.

The second experiment was to apply short current pulse to symmetric cell ($M|\text{MX}|M$) and measure generated concentration cell potential. If the distance between electrodes is much higher than product of salt diffusion coefficient and experiment time the investigated cell can be considered as the concentration cell $M|\text{MX}_1|\text{MX}_0|M$, so from the generated concentration potential one can calculate another slope of straight line taken into calculation for transference number determination.

2.5. FT-IR

Infrared absorption spectra were recorded on a computer-interfaced Perkin-Elmer 2000 FT-IR system with a wavenumber resolution of $\pm 2 \text{ cm}^{-1}$. FT-IR studies were performed at 25°C . Electrolytes were sandwiched between two NaCl plates and placed in the FT-IR temperature-controlled cell; the accuracy of the temperature was estimated to be $\pm 1^\circ\text{C}$.

3. Results

Fig. 1 presents changes in the bulk conductivity of polymeric electrolytes measured at 25°C as a function of LiClO_4 concentration and type of the filler used. At low salt concentrations (up to $10^{-2} \text{ mol kg}^{-1}$) as well as in the concentration range from 0.5 to 1 mol kg^{-1} conductivities measured for composite electrolytes are slightly higher than for pure PEODME-LiClO_4 system. At other salt concentrations studied ionic conductivities for pure and modified electrolytes are similar. Generally at almost all salt concentrations the highest conductivity has been achieved for composite electrolyte containing nanosize Al_2O_3 .

Addition of inorganic fillers leads to an increase in the glass transition temperature T_g of electrolytes observed for salt concentrations higher than 0.1 mol kg^{-1} (as can be seen in Fig. 2). At lower salt concentrations T_g values obtained for unmodified electrolyte are higher. At this salt concentration range the lowest T_g values are achieved for electrolytes containing self-prepared microsize fillers. At salt concentrations higher than 1 mol kg^{-1}

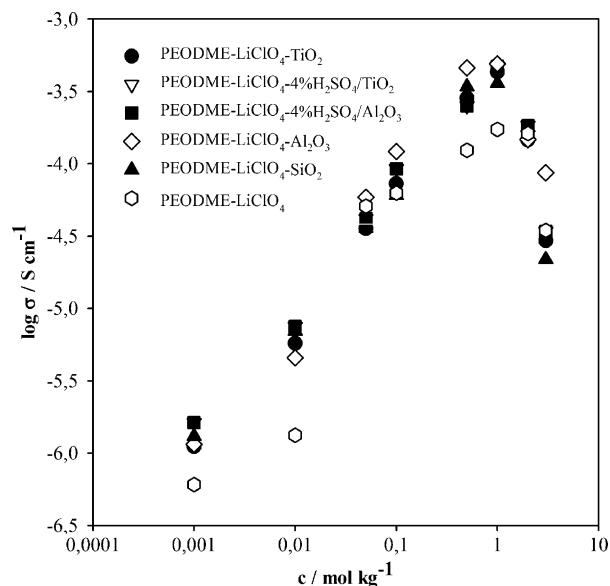


Fig. 1. Changes in ionic conductivity as a function of salt concentration obtained at 25°C for composite PEODME-LiClO_4 based electrolytes containing various inorganic additives. Comparison is made with the data obtained for the pristine PEODME-LiClO_4 electrolyte.

an increase in T_g is observed for all electrolytes studied which is due to the stiffening of polymeric host via intra or inter polymer chain crosslinks formed via ionic associates (most probably positively charged triplets) [16].

The later observation is consistent with IR studies of the position of C–O–C bond (see Fig. 3) characteristic for polymer–salt interactions. The shift of the position of the maximum of the C–O–C mode towards lower wavenumbers observed at salt con-

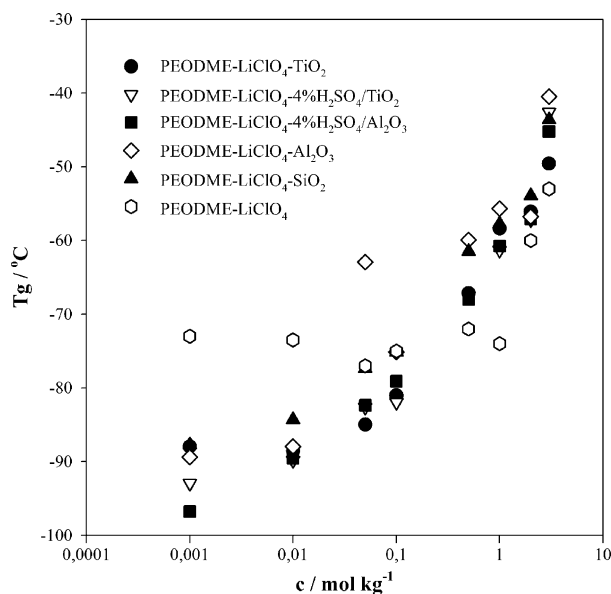


Fig. 2. Changes in glass transition temperature— T_g as a function of salt concentration obtained for composite PEODME-LiClO_4 based electrolytes containing various inorganic additives. Comparison is made with the data obtained for the pristine PEODME-LiClO_4 electrolyte.

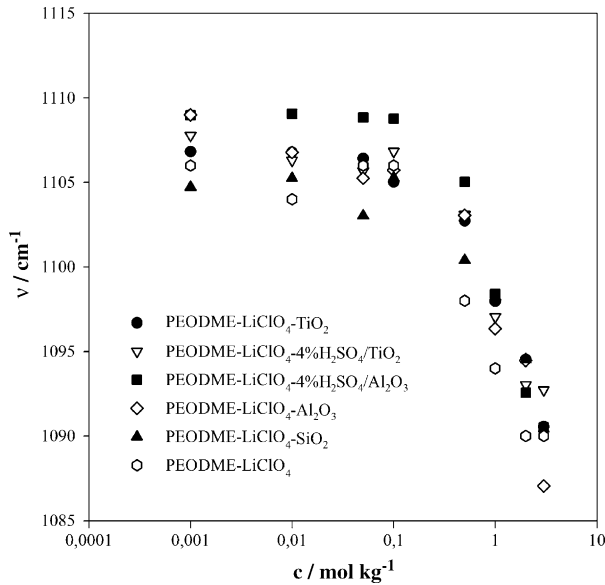


Fig. 3. Changes in the position of C—O—C IR vibration maxima as a function of salt concentration obtained at 25 °C for composite PEODME—LiClO₄ based electrolytes containing various inorganic additives. Comparison is made with the data obtained for the pristine PEODME—LiClO₄ electrolyte.

centrations higher than 0.5 mol kg⁻¹ confirms stiffening of the polymer hosts which results from the crosslinks formation. At lower salt concentrations position of the C—O—C mode maximum is between 110 and 1105 cm⁻¹ and do not change with salt concentration. IR studies also confirm interactions involving filler added. For most salt concentrations the position of the C—O—C mode for unmodified electrolyte is at lower wavenumbers suggesting stronger polymer—salt interactions which are weakened upon the addition of inorganic fillers. The strongest fillers—salt—polymer interactions seems to occur when the sulfonated alumina is used as an additive. This effect is particularly well seen at salt concentration above 1 mol kg⁻¹.

Fig. 4 presents comparison of the lithium transference numbers for PEODME—LiClO₄ and PEODME—LiClO₄—nanosize Al₂O₃ electrolytes.

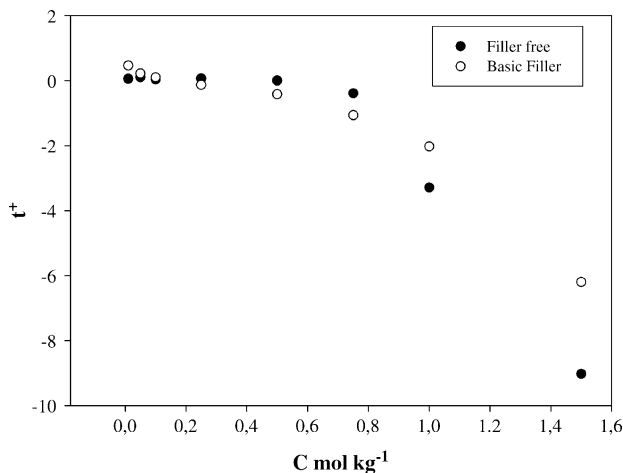


Fig. 4. Comparison of the lithium transference numbers measured as a function of salt concentration for PEODME—LiClO₄ and PEODME—LiClO₄—nanosize Al₂O₃ electrolytes.

Al₂O₃ electrolytes measured according to Newman's methodology [13,14]. For salt concentrations up to 1 mol kg⁻¹ lithium transference numbers for both electrolytes are similar. At higher salt concentrations lithium transference number obtained for composite electrolyte is much higher.

Impedance data over frequency range 1 MHz–1 Hz for samples of electrolytes sandwiched between lithium electrodes have been analyzed in Z'–Z'' co-ordinates as a series combination of parallel sub-circuits, each consisting of a resistor and a capacitive element. As the semi-arcs deviate from regular circles, constant phase element (CPE), characterized by admittance value Q and exponential coefficient n has been applied in the numerical fit procedure [17]. The semi-arc at higher frequencies is attributed to the properties of bulk electrolyte—conductivity and capacity of the electrolyte layer are expressed by the resistance R_e and CPE admittance Q_e , the latter approximating the capacity for a coefficient value of n close to 1. The value of the geometrical capacity calculated for this semicircle and $n=1$ is in the range 10⁻¹⁰ to 10⁻¹¹ F cm⁻² which are typical values obtained for polymeric electrolytes [18]. The semi-arc at lower frequencies represents the electrical parameters characterizing the lithium electrode polymer electrolyte interface: resistance R_{int} and capacity of the double layer, approximated by the admittance value of CPE Q_{int} . For these semicircle capacitances calculated for $n=1$ are within the range 10⁻⁷ to 10⁻⁸ F cm⁻² which are also typical values for capacitances describing interfacial phenomena [18].

Fig. 5 presents evolution of the impedance spectra measured for symmetrical lithium cell containing PEODME–2 mol kg⁻¹ LiClO₄–nanosize Al₂O₃ composite electrolyte. It is evident that the span of the second (lower frequency) semi-arc grew in time whereas the high frequency one remains almost invariant with time. The same behavior was found for other electrolytes studied despite those characterize by salt concentration equal to 10⁻³ mol kg⁻¹. For these electrolytes one semicircle was seen on impedance spectra span of which changed slightly in time. We attribute this semicircle to the bulk properties of the elec-

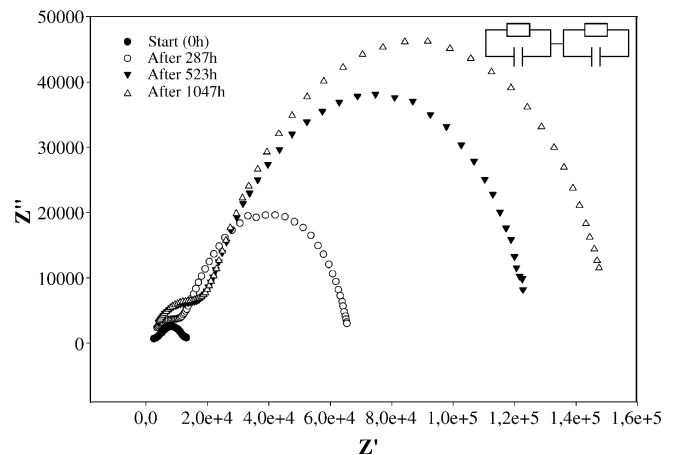


Fig. 5. C evolution of the impedance spectra obtained for the Li/PEODME—LiClO₄ (2 mol kg⁻¹)—Al₂O₃/Li symmetrical cell. The equivalent electrical circuit used for calculations of impedance parameters is shown as an insertion to the figure.

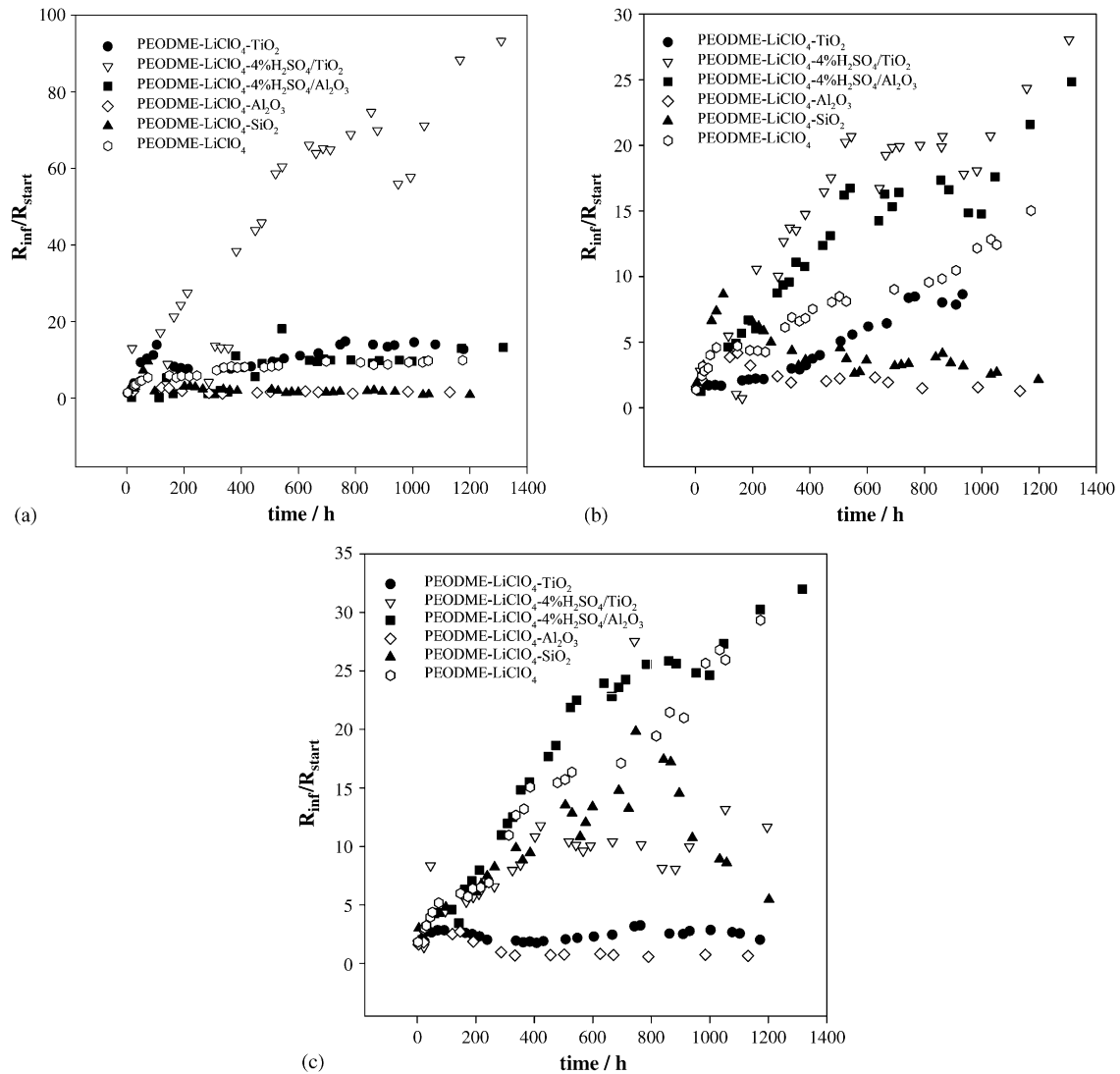


Fig. 6. Time evolution of the ratio of the electrode–electrolyte interfacial resistance to the initial electrode–electrolyte interfacial resistance (measured just after the completion of impedance cell) shown as a function of the type of filler used for electrolytes containing different concentration of LiClO_4 : (a) 0.5 mol kg^{-1} , (b) 1 mol kg^{-1} and (c) 2 mol kg^{-1} .

trolyte influenced by the initial formation of primary resistive layer at electrode–electrolyte interface.

Fig. 6a–c presents changes of the ratio of time dependent interfacial resistance to the initial interfacial resistance shown as a function of time for PEODME– LiClO_4 electrolytes containing different fillers for salt concentrations equal to 0.5 mol kg^{-1} (Fig. 6a), 1 mol kg^{-1} (Fig. 6b), 2 mol kg^{-1} (Fig. 6c). The data are compared to those obtained for PEODME– LiClO_4 electrolyte of the same salt concentrations. The electrolyte resistances were calculated using the Boukamp fitting procedure [17] on the basis of the equivalent circuit shown in Fig. 5. For salt concentration equal to 0.5 mol kg^{-1} only slight time increase in the resistance of electrode–electrolyte interface is seen. The changes are more visible only for composite electrolyte containing sulfonated titania. Interfacial resistance for unmodified electrolyte is amongst the lowest ones. More visible increase in the interfacial resistance is seen for systems with higher salt concentrations. For these electrolytes the highest increase in the interface resistance

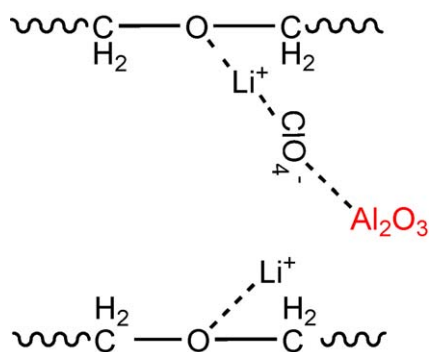
is observed for composite electrolytes containing sulfonated fillers and for unmodified PEODME– LiClO_4 electrolyte. At all salt concentrations the time stability of the interfacial resistance is the best for electrolyte containing nanosize Al_2O_3 .

4. Discussion

It has been shown that the addition of nano and microsize fillers may enhance the conductivity of polymer electrolytes doped with LiClO_4 . However, similar to our previous studies performed for composite system with alumina fillers bearing various surface groups the effect obtained is much less pronounced than for solid PEO based electrolytes or liquid poly(ethylene glycol) methyl ether (PEGME) derivatives [8]. Only in the very limited salt concentration range the increase in the conductivity was substantial as shown in Fig. 1. DSC and FT-IR studies confirmed interactions occurring between the added filler, salt and polymer matrix (see Figs. 2 and 3). Although in some

sense the observed trends were contradictory since T_g values shown stiffening of the polymer chains whereas IR studies of the position of the C–O–C mode suggest plasticizing effect of inorganic additives. Similar trends were previously observed in our studies on the effect of alkali metal cation on conductivity of perchlorate doped PEGME electrolytes [19]. Such behavior was previously discussed by McLin and Angell in their excellent paper [20]. According to their assumptions in low molecular weight unentangled polymers “viscosity can be expected to serve as a useful guide to the forces impeding the motion of ions present in the solution”. For high molecular weight polymers microviscosity described by the T_g is a parameter to be used. Based on these observations we have assumed that T_g is related to local polymeric motions at temperature far below conductivity experiments. At such a low temperature presence of bulky filler molecules may sterically hinder polymer segmental motion especially assuming high viscosity of low molecular weight system in this temperature range. FT-IR studies performed essentially at the same temperature range as conductivity determination is therefore much better correlated to conductivity data. Therefore, on the basis of IR observation we may assume that especially at high salt concentrations (above $\sim 0.5 \text{ mol kg}^{-1}$) the addition of filler results in the breaking of the crosslinks formed between polymeric chains most probably due to the interaction of filler molecules with perchlorate anion as shown in Scheme 1. As has been demonstrated by Frech and co-workers [16] the formation of crosslinking bonds via positively charged triplets is thermodynamically favorable. On the other hand most of the fillers used in these studies exhibit Lewis or Brønsted type acidity and therefore can react with perchlorate anions (acting as basic molecules) thus breaking the crosslink (as shown in Scheme 1) and increasing polymer chain flexibility (see IR data in Fig. 3). These type of interactions should lead to a release of lithium cations involved previously in the crosslink formation and thus to an increase in the cation transference number. This is indeed confirmed by the results of lithium transference number determination shown in Fig. 4. A considerable increase in lithium transference number is observed for composite system compared to PEGME–LiClO₄ electrolyte for salt concentrations higher than 0.5 mol kg^{-1} .

It has been also confirmed that the concentration of the dopant salt has an effect on the formation of interfacial layers and



Scheme 1. Breaking of the crosslinks formed between polymeric chains by the addition of acidic filler.

growth of their resistance in time. However, the addition of fillers results in the suppression of this growth compared to PEGME–LiClO₄ system. This effect was observed at salt concentrations higher than 1 mol kg^{-1} and for nanosize additives. Microsize sulfonated alumina and titania display higher rate of the growth of interfacial layer resistance than pristine polymer electrolyte. This may suggest that the contact surface area which might be much higher in the case of nanosize fillers may play a crucial effect in the filler interactions. The best interfacial stability is demonstrated for composite electrolyte containing nanosize alumina fillers. This leads us to the conclusions that in addition to filler surface area (which was the highest for SiO₂ filler) also the proper acidity of the filler is important. To support these suggestions further studies of filler with controlled surface area and acidity are needed.

5. Conclusions

It has been demonstrated that both the formation and growth of the resistive layers at the polymer electrolyte–lithium electrode interface is determined by the salt concentration range and depends also on the type of the filler used. For salt concentrations lower than $10^{-3} \text{ mol kg}^{-1}$ or higher than 1 mol kg^{-1} addition of filler results in the suppression of the growth of the resistance of the interfacial layer. This effect has been related to an increase in lithium cation transference number observed in these salt concentration ranges in composite electrolytes compared to the pure PEGME–LiClO₄ analogues [12]. The addition of fillers leads to an increase in the ionic conductivity of polymer electrolyte observed however in the limited salt concentration range. IR studies showed plasticizing effect of the added fillers which most probably results from breaking ionic crosslinks formed at high salt concentration range via positively charged triplets.

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