Short communication

The effect of salt concentration on the PEO–LiClO$_4$–lithium electrode interfacial resistivity

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Abstract

In the present paper the effect of the salt concentration on the formation and growth of the resistive layers at the polymer electrolyte–lithium electrode interface is analyzed. The studies are performed for poly(ethylene oxide)dimethyl ether (PEODME) doped with LiClO$_4$ electrolytes. It is shown that the rate of growth of the resistivity of interfacial layers depends on the concentration of the added salt and increases as the salt concentration increases. We have related this effect to the decrease in the lithium cation transference number and the increase in the fraction of ionic aggregates occurring with an increase in the salt concentration in polymeric electrolytes. The observed phenomena seem to be important from the viewpoint of application of polymeric electrolytes in lithium or (and) lithium ion batteries.
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1. Introduction

Polymer electrolytes are one of the most extensively studied groups of solid ionic conductors due to the possibility of their application in ambient and sub-ambient temperature lithium or lithium ion batteries [1,2]. The commercialization of batteries with polymeric electrolytes is however still a very challenging task due to their limited ionic conductivities, low cationic transport number and formation of resistive passive layers at the electrode–electrolyte interface of the time increasing resistance [3,4]. The growth of the passive layers is often connected with the predominant anionic conductivity of polymeric electrolytes. Basically, the high cation transference number is equally important for the practical application as the high conductivity value of the system [3]. The overall efficiency of the lithium cell is dependent both on the rate of charge transported by the electrodically active ion and on the resistance of the passive layer forming on the electrode surface as these phenomena lead to the internal voltage drops in the system. A good influence of high cation transference number can be observed for both of the above mentioned parameters.

The importance of understanding the nature of the formation and growth of resistive passive layers at the electrolyte–lithium electrode interface has been recognized and widely studied for liquid electrolytes used in lithium and lithium ion batteries [5,6]. There are also number of studies performed for gel and solid polymer electrolytes. Peled proposed a model of the Solid Electrolyte Interface applicable for polymeric electrolytes when in contact with lithium electrode [7,8]. The studies of the polymer electrolyte–lithium electrode interface were summarized by Scrosati and Neat in their excellent review paper [4]. Despite these intensive researches the structure of passive layers and the processes resulting in the growth of interfacial resistances are still under intensive studies [9–12].

It should be emphasized that most of the studies described in the literature were performed in the very limited salt concentration range. Usually high salt concentrations (around 1 mol kg^{-1} of the dopant salt) were applied. This salt concentration range corresponds to the practical limits used in lithium and/or lithium ion batteries. However, due to the limited salt concentration range it was relatively difficult to couple the resistivity of the interfacial layers formed with other properties characterizing ionic transport in polymeric electrolytes such as cation transport number and formation of ionic aggregates.

In the present work the effect of the salt concentration on the formation of the resistive passive layers at the polyether based polymeric electrolyte–lithium electrode interface is analyzed. The formation of interfacial passive layers is discussed in the relation to the lithium transference number of the electrolyte used as well as the formation of ionic associates. The above

studies are performed using mainly impedance spectroscopy in the wide frequency range. Conductivity studies are coupled to viscosity experiments, which help to determine ionic associations on the basis of the Fuoss–Krauss formalism [13,14]. The lithium transference number is measured using Newman's method adapted for liquid systems [15].

2. Experimental

2.1. Sample preparation

Poly(ethylene oxide)dimethyl ether (PEODME) ($M_W = 500$, Aldrich, dimethyl-capped, melting temperature equal to $-8\,°C$) was filtered, dried on a vacuum line at $\sim 60\,°C$ for 72 h, and then, under a 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. The salt concentration varied from 10^{-3} to 3 mol kg^{-1} of polymer. Samples with the salt concentration from 3 down to 0.5 mol kg^{-1} were prepared by the direct dissolution of the salt in a polymer. Samples of the highest salt concentrations were heated to $50\,°C$ to facilitate the dissolution process. Samples of lower salt concentrations were prepared by the successive dilution of a batch containing the electrolyte with 0.5 mol kg^{-1} of alkali metal salt. LiClO$_4$ (Aldrich, reagent grades) were dried under a vacuum of 10^{-5} Torr at $120\,°C$ prior to the dissolution.

2.2. Experimental techniques

2.2.1. Conductivity measurements

The impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range of 1 Hz–100 kHz. 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 reproducibility of impedance spectroscopy results was checked by the multiple experiments performed at room temperature. All results obtained for samples of the same composition did not differ by more than 10%.

2.2.2. AC impedance studies on Li/PEG–LiClO$_4$–electrolyte/Li cells

For these studies electrolytes were soaked on polypropylene textile separator of the 210 µm thickness. All electrolytes with complete LiClO$_4$ concentration range were studied. Prolonged AC impedance measurements in the 1 MHz–1 Hz frequency range with AC amplitude = 20 mV were performed. Duration of the experiments was equal to at least 2 months.

2.2.3. Lithium transference number determination

The details of the procedure used and description of the experimental set-up were described in our previous paper [16].

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 PEODME–LiClO$_4$ system the three independent species were chosen to be: Li$^+$, ClO$_4^-$ and PEODME, 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 symmetrical cell polarization.

To facilitate concentration cell experiments the special cell was designed by us [16]. The cell consists 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 symmetrical 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|PEO$_x$MX|PEO$_y$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 symmetrical cell (M|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|MX$_1$|MX$_0$|M, so from the generated concentration potential one can calculate another slope of straight line taken into calculation for transference number determination.

2.2.4. Rheological experiments

Rheological experiments were conducted at 25 °C using the Bohlin Visco 88BV viscometer in two coaxial cylinders geometry. The measurements were performed within a shear rate of 24–1200 cm^{-1}. The estimated error of rheological experiments is 10%.

3. Results

Fig. 1 presents changes of the molar conductivity of PEODME–LiClO$_4$ electrolytes as a function of square root of LiClO$_4$ concentration. The shape of the presented curve was discussed in details in our previous papers [17,18] and follows the original idea of Fuoss and Kraus who suggested three salt concentration regions in which ionic conductivity of weak elec-
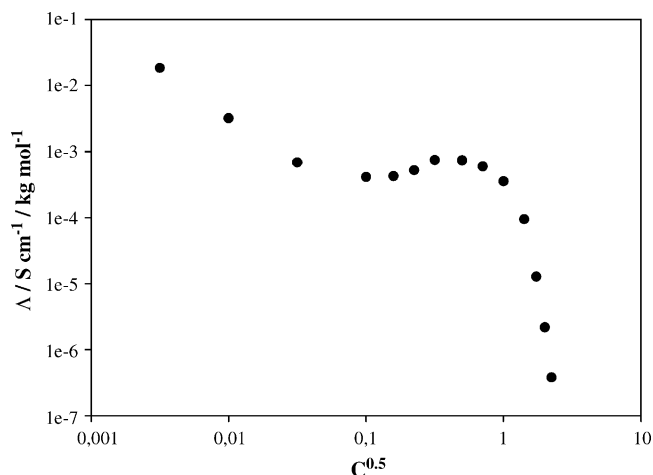
Fig. 1. Changes in the molar conductivity vs. square root of molar salt concentration for PEODME–LiClO$_4$ polymer electrolytes obtained at 25 °C.

trolytes depends on different ion transport phenomena. Hereby we would like to briefly describe the presented conductivity salt concentration dependence using Fuoss–Krauss approach. For salt concentration lower than ~10^{-2} mol kg^{-1} the decrease in molar conductivity with an increase in salt concentration is observed due to the increase in the fraction of ion pairs which as neutral species do not contribute to ionic transport. For this salt concentration range remaining free ions and ion pairs are dominant species present in the electrolyte. In the salt concentration range from 10^{-2} to ~1 mol kg^{-1} an increase in molar conductivity is observed due to the formation of charged ionic triplets. For higher salt concentrations the abrupt decrease in the conductivity is noticed. This is due to the increase in the electrolyte viscosity resulting from the formation of transient crosslinks preferably by linking one or more polymeric chains via positively charged triplets.

Fig. 2 presents changes in the lithium transport number and the fraction of ionic triplets as the function of salt concentration. The lithium transference numbers were calculated using Newman method as described in Section 2. The fraction of ionic triplets was calculated using the Fuoss–Krauss procedure pre-
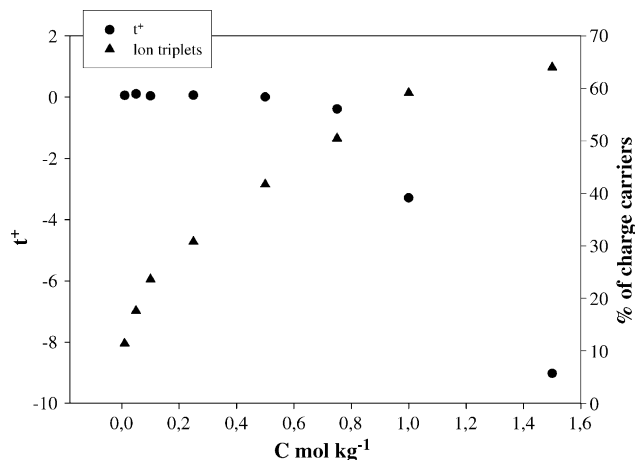

Fig. 2. Changes of the lithium transference number and fraction of ionic triplets as a function of salt concentration for PEODME–LiClO$_4$ polymer electrolytes.
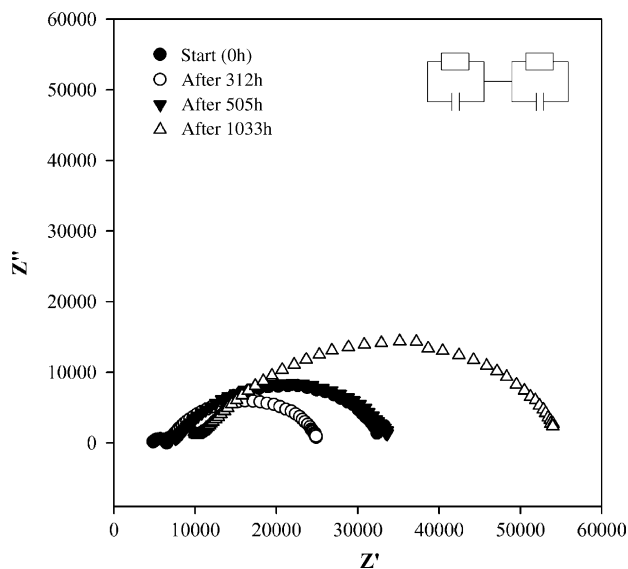

Fig. 3. Time evolution of the impedance spectra obtained for the Li/PEODME–LiClO$_4$ (2 mol kg^{-1})/Li symmetrical cell. The equivalent electrical circuit used for calculations of impedance parameters is shown as an inset.

viously adopted by Vincent and co-workers [19] and our group to polymeric electrolytes [20]. It is seen that anions are dominant mobile species in the electrolyte studied. It is particularly well seen for electrolytes with salt concentrations higher than ~0.5 mol kg^{-1} for which the lithium transference numbers are negative. By coupling this observation with the large fraction of ionic triplets calculated at this salt concentration range one may assume that the negatively charged triplets are dominant charge carriers at the salt concentration range which is usually used when applying polymer electrolyte in lithium batteries.

Fig. 3 presents evolution of the impedance spectra measured for symmetrical lithium cell containing PEODME–2 mol kg^{-1} LiClO$_4$ electrolyte. The impedance spectra shown in Nyquist coordinates consist of two depressed semicircles. It is evident that the span of the second (lower frequency) semicircle grew in time, whereas the high frequency one remains almost invariant with time. We have attributed the high frequency semicircle to the relaxation phenomena occurring in the electrolyte and low frequency one to the electrode–electrolyte interfacial behavior. Our assumption was based on the values of capacitance which were in the range 10^{-10} to 10^{-11} F cm^{-2} (for high frequency semicircles) and 10^{-7} to 10^{-8} F cm^{-2} (for low frequency semicircle). These are values typical for geometrical capacitance and capacitances describing electrode–electrolyte interfacial phenomena [21]. Therefore, the applied equivalent circuit consists of the series of two parallel combination of resistance with the frequency dependent capacitances as shown in Fig. 3(inset).

Fig. 4 presents changes of the ratio of time dependent electrolyte resistance to the initial electrolyte resistance as a function of time shown for PEODME–LiClO$_4$ electrolytes of various salt concentrations. The electrolyte resistances were calculated using the Boukamp fitting procedure on the basis of the equivalent circuit shown in Fig. 3 [22]. For sample with salt concentration equal to 1 mol kg^{-1} the electrolyte resistances remain almost invariant in time. An increase of the resistance was
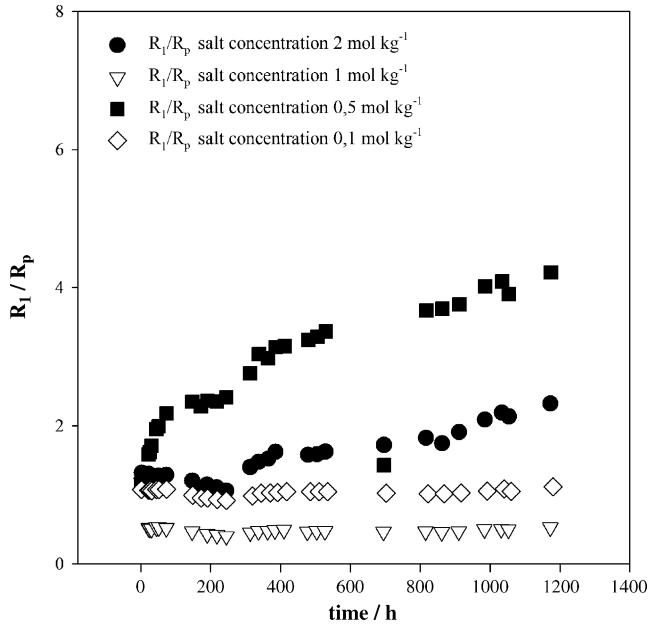
Fig. 4. Time evolution of the ratio of the bulk electrolyte resistance to the initial electrolyte resistance (measured just after the completion of impedance cell) shown as a function of dopant salt concentration for PEODME–LiClO$_4$ polymer electrolytes.

only observed for the sample with the lowest salt concentration -10^{-3} mol kg^{-1} (not shown on the graph). It should be emphasized that for this sample we were not able to separate two semicircles in the impedance spectra. Therefore, the initial increase in resistance maybe due to the formation of the primary passive layer (native layer [12]) at the electrolyte–electrode interface. For two electrolytes studied (samples with 0.5 and 2 mol kg^{-1} of salt) the change in resistance is also pronounced
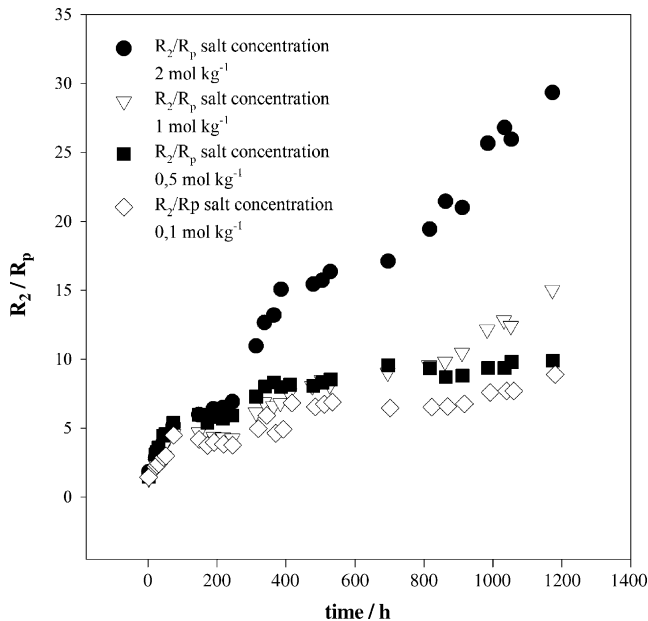

Fig. 5. Time evolution of the ratio of the electrode–electrolyte interfacial resistance to the initial electrode–electrolyte interfacial resistance (measured just after the completion of impedance cell) shown as a function of the LiClO$_4$ concentration.

(up to factor of 4 for the sample with 0.5 mol kg^{-1} of LiClO$_4$). This may suggest that the formation of interfacial layers may also result in the increase in overall bulk resistance of the electrolyte.

Fig. 5 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 with different salt concentrations. The resistances were calculated in the same way as described above for electrolyte resistances. It can be noticed that the growth of the resistance of the electrode–electrolyte interface is faster the higher is the salt concentration in the studied electrolyte. For salt concentrations up to 1 mol kg^{-1} the increase is up to 1 order of magnitude after 2 months of studies, whereas the ratio observed for the highest salt concentration exceeded 30 after the same period of time.

4. Discussion

The studies of lithium electrode–electrolyte interfacial behavior described in the literature revealed the complicated nature of the resistive passive layers formed at the interface. Despite various interpretations and often different and misleading nomenclature used by various research groups there are some similarities which can be generalized. The most important of these is the agreement on the fact that interfacial passive film does consist of several (at least two) layers of different nature of formation and growth. In his original work [8] Peled assumed that there is the formation of secondary porous layer on top of the primary Solid Electrolyte Interphase (SEI). This idea was further explored by Scanlon and co-workers [10] as well as Bouchet [11,12] who assumed the bilayer structure of interfacial passive films, primary of which is a native layer with resistance almost invariant in time and the secondary layer with resistance aging in time. Bouchet has shown [12] that the ionic transport through the interfacial layer is a rate determining step in the performance of the symmetrical lithium cell containing gel polymeric electrolyte as separator.

It is also of a common agreement that often the separation of contribution from various layers of interfacial films is difficult due to similar capacitances and time constants of the relaxation processes. In our present studies we do not manage to separate these contributions and therefore in the entire paper we refer to changes of the interfacial resistance as a whole. We manage to demonstrate however that the rate of growth of the resistance of the lithium electrode–polymer electrolyte interface depends on the concentration of salt used as an ionic dopant in polymeric electrolytes. This hence can be related to a decrease in the lithium transference number and an increase in the fraction of ionic aggregates (see Figs. 1 and 2). Assuming the model of lithium electrode–electrolyte interface developed by Peled [8] in which he postulated that "the secondary passive layer acts as a membrane which slows the mass transport of ions to SEI (being the primary layer)" it can be postulated that the lithium transference number has a crucial effect on the formation and growth of the secondary interfacial layers. For low salt concentrations in which lithium transference number is above zero and free ions

as well as ion pairs are dominant species lithium cation can relatively easily leave the electrode interface and after transportation through SEI get inside the bulk of the electrolyte. Moreover, the low electrolyte viscosity in this salt concentration range also facilitates the fast lithium transport. In this salt concentration range the only trap for lithium cations is the formation of ion pair when in contact with perchlorate anion.

On the other hand, for high salt concentrations (exceeding $1 \, \text{mol} \, \text{kg}^{-1}$), the electrolytes are highly viscous and negatively charged triplets are dominant mobile species. Therefore, it is highly probable for lithium cations when leaving the electrode and SEI to meet ionic aggregates and thus form quadruplets or higher orders ionic associates. These species are immobile in the highly viscous electrolyte and by trapping lithium cations contribute to the build up of the secondary layer and therefore the increase of the interfacial resistance. This observation is also consistent with studies by Bouchet [11,12] as well as our previous studies on the effect of poly(ethylene glycol)–poly(methyl methacrylate) blend composition on the interfacial resistance when these electrolytes are in contact with lithium electrode [23].

5. Conclusions

It is shown that the rate of growth of the resistivity of interfacial layers depends on the concentration of the added salt and increases as the salt concentration increases. We have related this effect to the decrease in the lithium cation transference number and the increase in the fraction of ionic aggregates occurring with an increase in the salt concentration in polymeric electrolytes. The observed phenomena seem to be important from the viewpoint of application of polymeric electrolytes in lithium or (and) lithium ion batteries.

Acknowledgement

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