

# Impedance and polarisation studies of new lithium polyelectrolyte gels

F. Krok<sup>a,\*</sup>, J.R. Dygas<sup>a</sup>, B. Misztal-Faraj<sup>a</sup>, Z. Florjańczyk<sup>b</sup>, W. Bzducha<sup>b</sup>

<sup>a</sup> *Institute of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland*

<sup>b</sup> *Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland*

## Abstract

Electrical conductivity, interaction with lithium metal and apparent  $\text{Li}^+$  transference number of gel polyelectrolytes was examined by the impedance spectroscopy and the dc polarisation of cells. Gel polyelectrolytes were obtained by crosslinking of plasticized lithium salts derived from comb-like half ester of maleic acid copolymer. Two gels contained additives: either  $\text{BF}_3$  as an agent complexing carboxylic anions or  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  salt as a source of additional lithium ions. The measured impedance spectra of cells  $\text{Li}/\text{gel}/\text{Li}$  were simulated by an equivalent circuit. The time evolution of the circuit parameters indicated growth of passivation layer and degradation of the electrolyte. In all studied gels, the apparent  $\text{Li}^+$  transference number had low values, which decreased upon time of storage of cells with lithium electrodes. Probably small ions are formed upon chemical interaction between lithium and dimethoxyethylenesulfoxide—the polar solvent used as a plasticizer. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Gel polyelectrolytes; Impedance spectroscopy; dc polarisation; Transference number; Interface passivation; Equivalent circuit

## 1. Introduction

Polyelectrolytes with immobilised anions and mobile lithium cations are very interesting candidates as electrolytes in lithium batteries and other electrochemical devices. The ionic conductivity of solid polymeric lithium salts is too low for application in lithium rechargeable batteries. Many attempts were undertaken to obtain high conductivity in such systems [1]. Addition of liquid polar solvent capable of solvating lithium ions and plasticizing the system leads to conductivity increase. The gel polyelectrolytes obtained in this way have in principle only cations mobile. In that respect, they are different from polymer gel electrolytes [2] which have both anions and cations mobile. The conductivity of gel systems is much higher than in the non-plasticized polymers. Apart from high conductivity, the stability against lithium metal anode is a vital requirement for application. Presence of the polar plasticizer may be a source of the instability upon contact of the gel with lithium metal.

We report investigation of gel polyelectrolytes based on solvent plasticized polymeric lithium salt derived from

comb-like half ester of maleic acid copolymer with immobilised carboxylic anions. A new polar solvent—dimethoxyethylenesulfoxide was used as plasticizer. In two of these systems additives were introduced: in one a Lewis acid— $\text{BF}_3$ , in the other an inorganic salt— $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ . The gel polyelectrolyte without additives was expected to exhibit the  $\text{Li}^+$  transference number close to one.  $\text{BF}_3$  was used as an agent complexing the carboxylic anions. Based on the IR and the  $^7\text{Li}$  NMR studies [3,4], it was found that after complexation with  $\text{BF}_3$  the carboxylic anions were separated from the lithium cations, which facilitated the dissociation of the polymeric salt and caused a significant increase of the conductivity. Addition of the inorganic salt was made on purpose to study its influence on the  $\text{Li}^+$  transference number and on the ionic conductivity. The lithium salt was a source of additional  $\text{Li}^+$  cations and inorganic anions, making the system similar to a polymer gel electrolyte with both cations and anions mobile.

The ionic conductivity and the interaction of gel polyelectrolytes with the lithium metal were studied by the impedance spectroscopy. The  $\text{Li}^+$  transference number was evaluated by the combined dc and ac methods [5]. Preliminary results on polyelectrolyte gel without additives and on the system complexed with  $\text{BF}_3$  have been reported in Ref. [6]. Here the main attention is paid to the system with the inorganic salt and its comparison with the other two.

\* Corresponding author. Tel.: +48-22-6296124; Fax: +48-22-6282171; E-mail: fkrok@mp.pw.edu.pl

## 2. Experimental

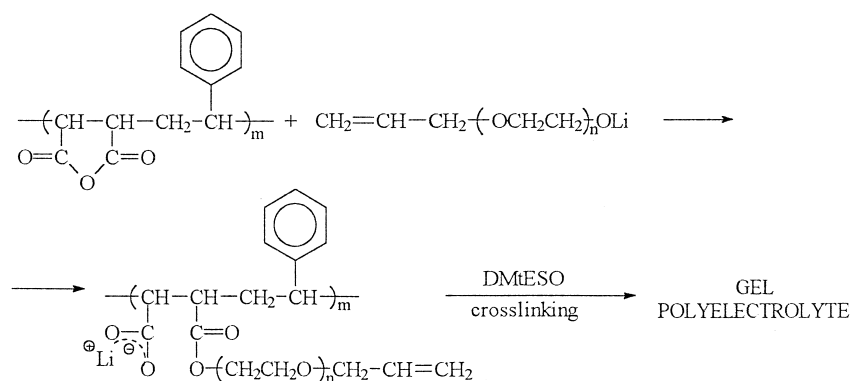
### 2.1. Gel preparation

An alternating maleic anhydride and styrene copolymer of molecular weight  $M_n \approx 3.2 \times 10^5$  was used as the initial polymeric product for the synthesis of polyelectrolytes. The copolymer was obtained by free radical copolymerisation carried out at  $60^\circ\text{C}$  in toluene. The poly(ethylene oxide) glycol terminated by an allyl group was obtained by anionic polymerisation of ethylene oxide in allyl alcohol according to the general method described elsewhere [7].

A solution of the copolymer (0.5 g) in  $15\text{ cm}^3$  of dimethylsulfoxide (DMSO) was added drop-wise to an equimolar amount of poly(ethylene glycol) alcoholate obtained from corresponding glycol and *n*-butyllithium ( $\sim 25\text{ mmol}$  in  $15\text{ cm}^3$  of DMSO). The reaction course was controlled by measuring the intensity of bands of the  $\text{C}=\text{O}$  bonds stretching vibrations at  $1770\text{ cm}^{-1}$  (in anhydride groups) and at  $1720\text{ cm}^{-1}$  (in ester groups).

The electrolyte solution in DMSO was poured onto acidified water. The precipitated polymer was filtered off and purified by dissolution in methanol and precipitation in water. Finally, the acidic form of the electrolyte (0.2 g) was dissolved in  $5\text{ cm}^3$  of absolute methanol and converted into a salt by dropping in solutions of lithium methanlates. Appropriate amounts of plasticizer, free radical initiator and, in some cases, equimolar amount of  $\text{BF}_3$  with respect to the carboxylic groups in the polymer matrix or 5 wt.% of salt  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , were added to the solution. A thin layer was poured out and methanol was removed. Gels were obtained by thermal crosslinking at  $70^\circ\text{C}$  for  $\sim 1\text{ h}$ . Polyelectrolyte gels obtained from Scheme 1 of average number  $n \approx 3.5$  contained 50 wt.% dimethoxyethylenesulfoxide (DMtESO)  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{S}(\text{O})\text{CH}_2\text{-CH}_2\text{OCH}_3$  [6] as plasticizer.

Three kinds of gels were studied: (a) gel A without additives; (b) gel B in which carboxylic groups were complexed by an equimolar amount of  $\text{BF}_3$ ; and (c) gel C containing 5 wt.% of inorganic salt  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ .



Scheme 1.

### 2.2. Electrical measurements

The Li/gel polyelectrolyte/Li cells and cells with stainless steel electrodes were studied by the impedance spectroscopy and the dc polarisation method. The cells were encapsulated in gas tight containers and placed in thermostated chambers.

The Solartron 1260 was used for impedance measurements. Amplitude of the ac signal was 7 mV rms, the frequency range was typically from  $10^7$  to  $10^{-2}\text{ Hz}$ , sometimes extended to  $10^{-3}\text{ Hz}$ . Impedance spectra were analysed by the non-linear least squares fitting of equivalent circuits. The polarisation current was monitored with the Solartron 1286 Electrochemical Interface, which was coupled to the Solartron 1255 for the impedance measurements performed with the dc polarisation applied to the cell. The method proposed by Evans et al. [5] was applied to determine the transference number  $t_{\text{Li}^+}$  of  $\text{Li}^+$  ions using symmetrical cell with Li electrodes.

The cells Li/gel/Li were stored for up to 700 h (gel A, gel B) or 1400 h (gel C) at constant temperature  $30^\circ\text{C}$  and the impedance spectra were measured at various time intervals. The transference number determinations were carried out on fresh cells, within a couple of days after assembling, as well as on aged cells after 3 to 7 weeks of storing at  $30^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Electrical conductivity

The temperature dependence of the conductivity determined by the impedance measurements of cells with stainless steel electrodes is shown in Fig. 1. The conductivity of gel A was  $\sim 10^{-5}\text{ S cm}^{-1}$  at  $20^\circ\text{C}$  and was significantly lower than conductivity of the other two gels in the entire temperature range from  $-30^\circ\text{C}$  to  $80^\circ\text{C}$ . The addition of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ —gel C, caused an increase of the conductivity nearly by one order of magnitude. Taking into account that gel A contains mobile  $\text{Li}^+$  cations, while the

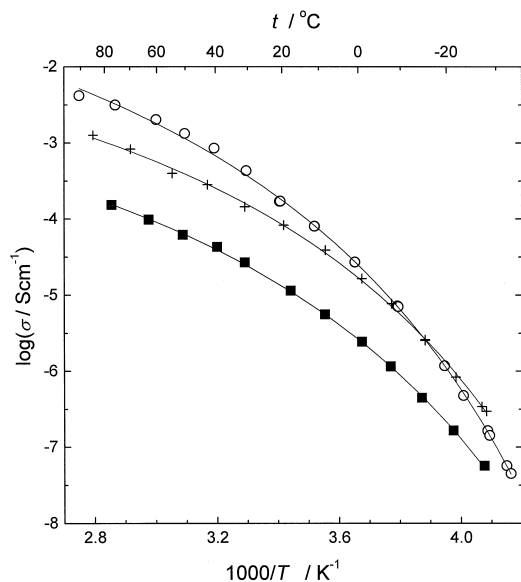


Fig. 1. Temperature dependence of the conductivity of gel polyelectrolytes based on Scheme 1: (■) gel A, (○) gel B complexed with  $\text{BF}_3$ , (+) gel C containing 5 wt.%  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ . Continuous lines represent the fitted VTF dependence.

anions are immobilised, the large increase of the conductivity upon addition of inorganic salt seems to be due to introduction of mobile anions. Thus, it may be expected that gel C is predominantly anion conductor. In the case of gel B the electrical conductivity was even higher than in the case of gel C. Based on IR and  $^7\text{Li}$  NMR studies [3,4], the increase of conductivity upon complexation with  $\text{BF}_3$  is interpreted by formation of the co-ordination bond between boron atoms and oxygen atoms of the carboxylic

group, which leads to the separation of lithium cations from carboxylic anions and an increase of the  $\text{Li}^+$  cations mobility.

The temperature dependence of the conductivity of the studied systems was well reproduced by the VTF equation  $\sigma(T) = aT^{-1/2} \exp[-b/(T - T_0)]$ . The fitted values of  $T_0$ : 182 K for gel A, 187 K for gel B and 185 K for gel C were close to the glass transition temperatures determined by the DSC.

### 3.2. Interaction of gel polyelectrolytes with lithium

The complex plane diagrams of impedance of Li/gel/Li cells consisted of two depressed arcs and a spur inclined at an angle close to  $45^\circ$  emerging at the lowest frequencies. In Fig. 2, examples of the impedance diagrams for gel C are shown for different storage times. The impedance diagrams for the two other gels were similar to those shown in Fig. 2, apart from the fact that for gel A the impedance was dominated by the large arc at high frequencies while for gel B by the large arc at low frequencies. The two arcs and the spur were well separated and two values of resistance could be obtained from the diagrams:  $R_b$  interpreted as the resistance of the bulk of electrolyte and  $R_c = R_b + R_i$  the sum of  $R_b$  and the interfacial resistance  $R_i$ .

The time dependence of the apparent bulk conductivity  $\sigma = l/(SR_b)$  of the electrolytes in Li/gel/Li cells, see Fig. 3a, was different for gel B than for the other two systems. Conductivity of gel A and gel C decreased rapidly during the first 50 h after assembling of the cell and continued to decrease with a lower rate, reaching at the end of the experiment values nearly 10 times lower than

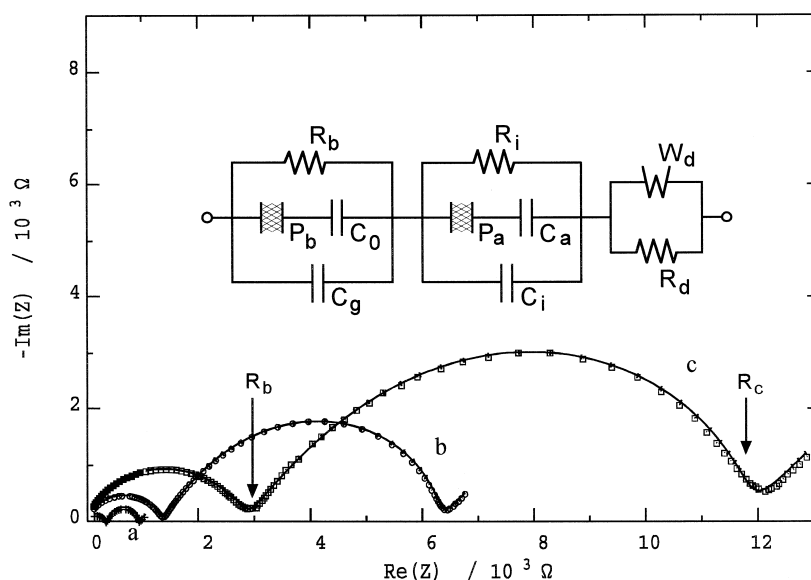


Fig. 2. Evolution with time of the impedance of the Li/gel C/Li cell at constant temperature  $30^\circ\text{C}$ : (a) 5 h, (b) 314 h, (c) 1204 h after assembling. Frequency range  $10^7$  to  $10^{-2}$  Hz. Continuous lines represent the fitted impedance of the equivalent circuit shown in the insert. Cross hatched capacitors denote the cpe elements,  $W$  is the Warburg infinite diffusion impedance.

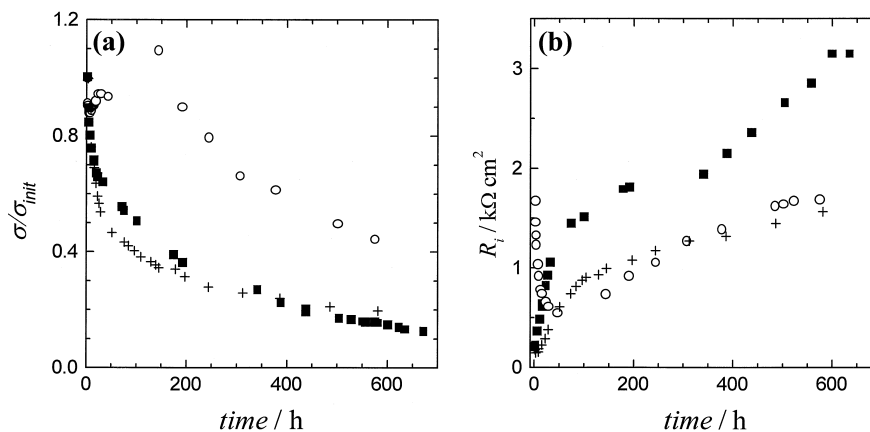


Fig. 3. Dependence of the resistive components of the impedance of cells Li/gel/Li on the time of storage at 30°C: (■) gel A, (○) gel B, (+) gel C. (a) Relative values of the bulk conductivity of polyelectrolyte gels—each value of the conductivity is divided by the initial value of conductivity measured after assembling of the given cell. (b) The interfacial resistance  $R_i$  multiplied by the area of electrode.

initial. It indicates that a passivation layer is formed inside the electrolyte or the entire polymeric membrane undergoes degradation upon contact with lithium. It is likely that small anions are formed upon contact of the solvent (DMtESO) with the lithium metal, which inhibits solvation of lithium ions and leads to stiffening of the gel. In the case of gel B, initial increase of the conductivity was followed by a slow decrease. The degradation of electrolyte is inhibited by the presence of  $BF_3$ , which probably takes part in formation of the passive layer on the lithium surface and inhibits the reaction between lithium and solvent.

The time dependence of the interface resistance  $R_i$  is also different for gel B than for the other two gels (see Fig. 3b). The  $R_i$  of Li/gel/Li cells with gel A and gel C increases rapidly during the first  $\sim 100$  h and then grows at a slower pace. After  $\sim 100$  h, the interfacial resistance in cell with gel A is about twice larger than in cells with the other two gels. In the case of gel B, the  $R_i$  is initially large and decreases, then after  $\sim 50$  h of contact between lithium and gel starts to increase, reaching at the end of the experiment similar values as in the case of gel C.

For all studied Li/gel/Li cells the measured impedance spectra could be well reproduced by the impedance of the equivalent circuit shown as an insert of Fig. 2. The circuit is composed of resistors, capacitors and constant phase elements—cpe, whose complex admittance was expressed as:  $Y(\omega) = A(j\omega)^{1-N}$ . The Warburg infinite diffusion impedance,  $Z_w(\omega) = W(j\omega)^{-1/2}$ , is equivalent to a cpe with the exponent  $N = 0.5$ .

The left part of the circuit represents the bulk of the electrolyte and has the same form as the corresponding part of the equivalent circuit used to model the impedance of cells with stainless steel electrodes. The branch of the equivalent circuit, consisting of the cpe  $P_b$  and capacitor  $C_0$ , simulates the frequency dependence of the ionic conductivity and the electric permittivity of the gel. The fitted

values of the cpe exponent  $N_p$  were between 0.4 and 0.55 for the investigated gels.

The central section of the circuit represents the interface between the gel electrolyte and the Li electrode. It has three parallel branches: (i) the interfacial resistance  $R_i$ ; (ii) the cpe  $P_a$  in series with capacitance  $C_a$ ; (iii) the capacitor  $C_i$ . The estimated values of the cpe exponent were  $N_a \cong 0.5$ , except for the spectra measured during the initial period of the rapid change of the interfacial impedance. Similar equivalent circuit was used by Churikov et al. [8] to model the passive films on the surface of lithium alloys in liquid electrolytes based on propylene carbonate. According to the interpretation proposed by Churikov et al., which is plausible also in the present case, the circuit represents the passivation film:  $C_i$  is the geometric capacitance of the film,  $R_i$  the resistance of the film,  $P_a$  in series with  $C_a$  models the diffuse double layer–space charge region in the film.

In the right part of the circuit of Fig. 2, the Warburg element  $W_d$  reproduces the low frequency spur in the impedance diagrams which is associated with the diffusion in the electrolyte when mobile cations and anions are present. In the case of spectra extending to frequencies below  $10^{-2}$  Hz, the resistance  $R_d$  added parallel to the Warburg element  $W_d$  improved the quality of fit.

The time dependence of all components of the equivalent circuit in the case of gel C is presented in Fig. 4. The increase of the Warburg constant  $W_d$  closely resembles changes of the bulk resistance  $R_b$  (Fig. 4a). The interfacial resistance  $R_i$  changes in accord with the Warburg constant  $W_a$  assigned to the  $Li^+$  diffusion in the passivation film (Fig. 4b). The capacitances  $C_i$  and  $C_a$  decrease rapidly during the first  $\sim 100$  h, which indicates the period of growth of the thickness of the passivation film. Later, they level off at values:  $C_a \cong 15 \mu F cm^{-2}$  and  $C_i \cong 1 \mu F cm^{-2}$ , that are in accord with the interpretation given above.

### 3.3. $\text{Li}^+$ transference number

The results obtained by combination of the dc polarisation and ac impedance methods are summarised in Table 1. The measured current fractions,  $I_s/I_o$  ( $I_o$ —initial current,  $I_s$ —steady-state current), agree well with the  $\text{Li}^+$  transference numbers evaluated according to the formula introduced by Evans et al. [5] only in the case of cells with gel A, whose bulk resistance was much higher than the interfacial resistance. In the case of gel B and gel C, the apparent

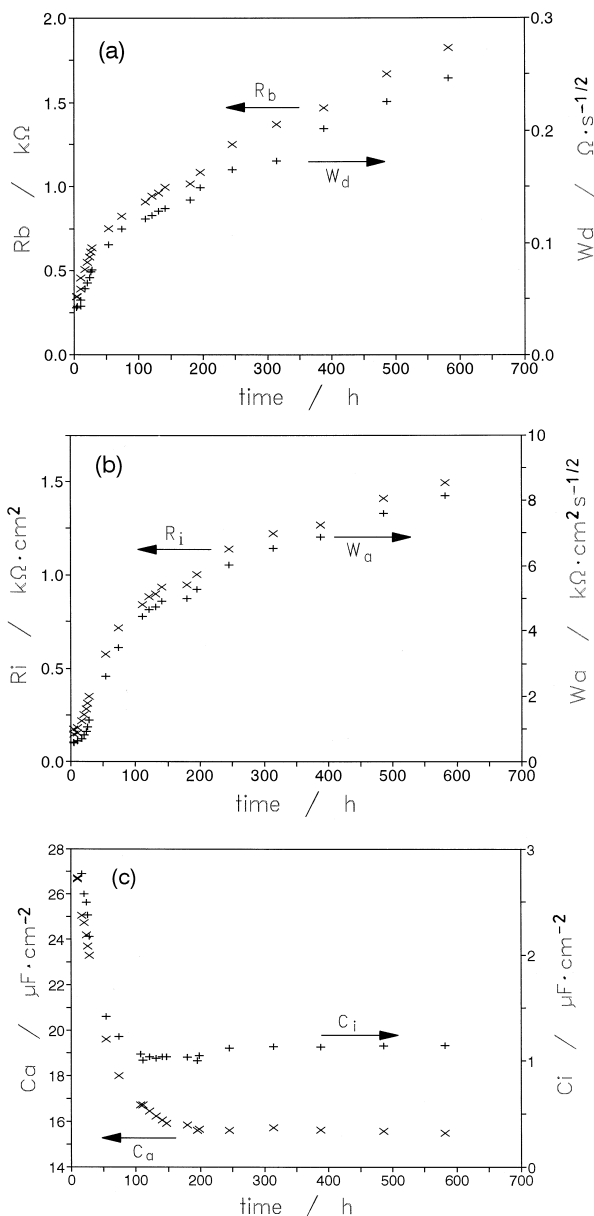


Fig. 4. Dependence of parameters of the equivalent circuit of Fig. 2 on the time of storage at 30°C of the cell Li/gel C/Li: (a) the bulk resistance  $R_b$  and the Warburg constant  $W_d$ ; (b) the interfacial resistance  $R_i$  and the Warburg constant  $W_a$  (multiplied by area of the interface); (c) capacitance per unit area of the passivation film  $C_i$  and of the diffuse double layer  $C_a$ .

Table 1

Current fractions  $I_s/I_o$  and the apparent  $\text{Li}^+$  transference numbers  $t_{\text{Li}^+}$  for gel polyelectrolytes in the freshly assembled and aged Li/gel/Li cells

Polyelectrolyte	Gel A	Gel A	Gel B	Gel B	Gel C	Gel C
Time of storage (h)	24	576	24	480	76	1163
$I_s/I_o$	0.29	0.14	0.62	0.58	0.29	0.16
$t_{\text{Li}^+}$	0.24	0.12	0.14	0.10	0.08	0.04

transference numbers, which take into account the voltage drop over the Li/electrolyte interface, are approximately four times lower than the respective current fractions. Taking into account that the evaluation of the ionic transference number in polymer electrolytes by the dc/ac method is limited by several factors [9], we treat the obtained values with caution, but believe that the observed trends are real. For the three studied gels, the  $\text{Li}^+$  transference number determined for freshly assembled cells is greater than for cells stored several weeks. This finding correlates well with the proposition that small anions are formed in the gel upon interaction between solvent and lithium.

## 4. Conclusions

The studied polyelectrolyte gels exhibit high ionic conductivity in cells with stainless steel electrodes but undergo degradation in cells with lithium electrodes.

Passivation film of growing resistance is formed on the surface of lithium. The impedance of cells Li/gel polyelectrolyte/Li was modelled by the equivalent circuit that allowed insight in the process of passivation. The formation of the passivation film is modified by the addition of  $\text{BF}_3$ , which inhibits degradation of the polyelectrolyte gel.

Chemical interaction between the plasticizer (DMtESO) and lithium results in the decrease of the bulk conductivity of the gel electrolyte, accompanied by the decrease of the  $\text{Li}^+$  transference number, probably due to formation of small anions. However, it remains likely that, prior to contact with lithium, the gels without addition of an inorganic salt are single ions conductors.

The studied polyelectrolyte gels are not suitable for use with lithium metal due to the reactivity of the polar solvent used. This polymeric salt, based on the investigated Scheme 1, may remain attractive for applications if less reactive plasticizer can be found.

## Acknowledgements

Financial support for this project from the Polish State Committee for Scientific Research (grant 8 T10C 048 15) is gratefully acknowledged.

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