

Short communication

Physico- and electrochemistry of composite electrolytes based on PEO-DME–LiTFSI with TiO₂

M. Moskwiak, I. Giska, R. Borkowska, A. Zalewska*, M. Marczewski, H. Marczewska, W. Wieczorek

Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warszawa, Poland

Available online 3 April 2006

Abstract

The effect of fumed TiO₂ fillers (pure and modified by H₂SO₄) on ionic conductivity of composite electrolytes based on poly(ethylene oxide) dimethyl ether (PEODME) oligomer ($M_w = 500$) doped with lithium bis-(trifluoromethanesulfonyl)imide LiN(CF₃SO₂)₂ (LiTFSI) are studied by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR) and complex impedance methods. The electrochemical stability of the electrolytes in the potential range of 4 V versus Li electrode has been confirmed by voltammetric measurements. Li electrode reactions have been followed by means of impedance spectroscopy. The growth in time of the resistance of the interfacial (Li electrode–polymer electrolyte) layers was inhibited upon the addition of fillers.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Poly(ethylene oxide) dimethyl ether (PEODME); Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI); Composite polymer electrolyte; TiO₂ pure and modified by H₂SO₄; Conductivity; Lithium cell

1. Introduction

Polymer electrolytes have been investigated due to the possibility of their application in a variety of electrochemical devices working from subambient to moderate temperature range [1,2]. A lot of work related to ionically conducting polymer matrices present in the literature are devoted to complexes of poly(ethylene oxide) (PEO) or modified PEO with alkali metal salts. The properties of polyether based polymer electrolytes have been modified from the viewpoint of their application. Methods of modification which use inorganic fillers, such as silica, zeolites, titanium or aluminum oxides as additives, offer same advantages compared to the other routes of modifications [1,2]. Addition of inorganic fillers results in improved ionic conductivity, extended thermal stability range, better electrochemical stability and compatibility between electrolyte and electrode as reviewed by Zhou and Fedkiw [3].

Another promising method to enhance the ionic conductivity of crystalline polyether electrolytes is to incorporate lithium salts with a large anion such as lithium bis-

(trifluoromethanesulfonyl)imide (LiTFSI) which are expected to lower the crystallization of PEO–LiTFSI complexes and enhance the conductivity [4,5]. The addition of salts having large anions with dispersed charged also results in reducing fraction of ionic associates which hence leads to an increase in the cation transport number.

The effect of fumed oxide filler (SiO₂, Al₂O₃, TiO₂) on ionic conductivity of composite electrolytes based on PEO oligomers with LiTFSI has been studied by Zhou and Fedkiw [3]. It was shown that the addition of fillers stiffens polymer segments and no reduction in ion pairing is observed. Our previous studies showed [6] that besides the size of inorganic filler also the type of surface groups has an important effect on ion–ion and ion–polymer interactions. The addition of fillers with Lewis acid surface groups usually leads to the reduction in ion pairing and therefore to an increase in the conductivity. This is due to the interactions of acidic filler centers with anions being considered as Lewis bases. These interactions lead to the release of cations from ion pairs and higher aggregates and therefore to an increase in the cation transport numbers as confirmed by the studies of Scrosati's group [7,8]. However, it has been also noticed that the addition of a strong Lewis acid often leads to the degradation of polymeric chains [9]. Therefore, according to the procedures commonly use in chemical catalysis we decided to soften the

* Corresponding author. Tel.: +48 22 6605739; fax: +48 22 6282741.
E-mail address: aldona@ch.pw.edu.pl (A. Zalewska).

later effect by the attachment of a strong acid group to the inert filler support.

In the present paper the effect of fumed oxide fillers TiO_2 pure and modified with H_2SO_4 on the ionic conductivity of a composite electrolyte based on PEO/DME with LiTFSI as a dopant are studied by differential scanning calorimeter (DSC), Fourier transform infrared spectroscopy (FT-IR) and complex impedance method. We have used low-molecular weight polyether analogues to obtain single phase amorphous systems at ambient temperatures and limit possible side effects due to the crystallization of the polymer matrix. The electrochemical stability window of the electrolytes in the potential range of 4 V has been confirmed by voltammetric measurements. Li electrode reactions have been followed by means of impedance spectroscopy technique.

2. Experimental

2.1. Sample preparation

PEODME ($M_w = 500$, Aldrich) was filtered and dried on a vacuum line 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. The salt content was ranging from 1 to 5 mol kg^{-1} of polymer.

$\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI) (Aldrich, reagent grade) was dried under vacuum at 120°C prior to dissolution. The composite electrolytes were obtained by the dispersion of TiO_2 in a PEO/DME–LiTFSI solutions. The concentration of TiO_2 in the composite electrolytes was equal to 10 mass% of the PEO/DME.

Two types of TiO_2 fillers of different grain sizes were used as additives. Plain TiO_2 of the size equal to 21 nm and surface modified TiO_2 (P 25, Degussa) which was used as acid group carrier. The initial grain size of the latter powder was roughly 0.4–0.6 μm . The surface modification was performed by impregnating particles with aqueous solutions of H_2SO_4 whose concentrations were calculated to obtain mixtures containing 4 wt% of the acid [10]. (The acidity of the obtained fillers is higher than for H_2SO_4 itself and such systems are often named superacids in chemical catalysis.) Then grains were milled in mortar and sieved in order to obtain a homogeneous thin powder (average size of about 10 μm). Fillers were then dried under vacuum of 10^{-5} Torr at 150°C for 72 h prior to addition to the polymer–salt mixture. The sulfonated filler preparation procedure differed slightly from those applied in our previous studies [11].

2.2. Impedance spectroscopy

Ionic conductivity was determined using the complex impedance method in the temperature range from -20 to 70°C . The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature controlled oven. Experiments were performed in a constant-volume cylindrical cell with

an electrode diameter of 7.8 mm and fixed electrolyte thickness of 1.6 mm. The cell was placed in a glass vacuum chamber which was evacuated at 10^{-2} Torr for 2 h prior to the experiments. The impedance spectroscopy studies were carried out under static vacuum.

The same conditions were applied at room temperature for the investigations of Li/electrolyte/Li symmetric cells. The impedance spectra were registered over a long time period (150 h). All impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the frequency range from 1 Hz to 1 MHz. The reproducibility of impedance spectroscopy results was checked by multiple experiments performed at room temperature and analyzed in comparison with typical equivalent circuit proposed in previous studies [12]. The results obtained for samples of the same composition do not differ by more than 10%.

2.3. FT-IR

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

2.4. DSC studies

DSC experiments were performed on Perkin-Elmer Pyris 1 scanning calorimeter equipped with a low temperature measuring head and liquid-nitrogen-cooled heating element. Samples in aluminum pans were stabilized by slow cooling to -90°C and then heated at $20^\circ\text{C min}^{-1}$ to 30°C . An empty aluminum pan was used as a reference. The estimated error of the determination of the glass transition temperature (T_g) is $\pm 2^\circ\text{C}$.

3. Results and discussion

Fig. 1 shows the isotherms of ionic conductivity of PEO/DME–LiTFSI electrolytes without and with 10 mass% of TiO_2 or $\text{TiO}_2/\text{H}_2\text{SO}_4$ additives measured at -20 , 20 and 50°C as a function of salt concentration. Ionic conductivity isotherms measured at 20 and 50°C do not show any differences between samples; the filler does not have a significant effect on conductivity. The conductivity decreases with increasing lithium salt concentration. The same situation is observed for isotherm measured at -20°C for samples containing 3, 4 or 5 mol kg^{-1} LiTFSI. For samples with 1 and 2 mol kg^{-1} of lithium salts we have observed variation in conductivity depending on sample compositions. For these samples the crystallization process was observed at ~ 0 – 6°C range. Therefore, the drop in the conductivity observed in Fig. 1 can be explained by the presence of crystalline polymeric phases.

Fig. 2 presents ionic conductivity of PEO/DME–(1 mol kg^{-1}) LiTFSI without and with 10 mass% of TiO_2 or $\text{TiO}_2/\text{H}_2\text{SO}_4$ measured at low temperature range. At temperatures lower than 10°C the highest conductivity has been measured for samples

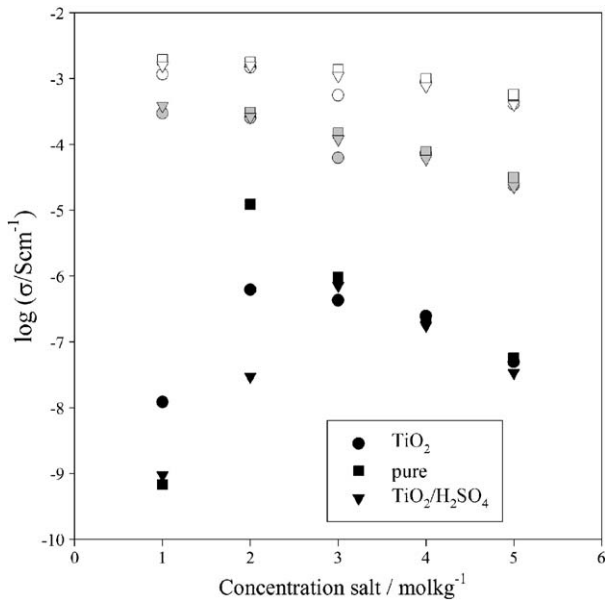


Fig. 1. Isotherms of ionic conductivity of PEODME–LiTFSI without and with 10 mass% of TiO_2 or $\text{TiO}_2/\text{H}_2\text{SO}_4$ composite polymeric electrolytes measured at -20°C (black color), 20°C (grey color) and 50°C (white color) as a function of salt concentrations.

with unmodified TiO_2 . At these temperatures conductivities measured for pristine PEODME–LiTFSI sample and that with modified TiO_2 are similar. Conductivities measured for all three systems at temperatures higher than 10°C are very close to each other. Such behavior should be attributed to the presence of the crystalline phase at temperatures lower than $\sim 10^\circ\text{C}$ for samples of this salt concentration. Therefore, the addition of filler results mainly in the suppression of the electrolyte crystallinity. As demonstrated in a variety of previous studies this effect should be more pronounced for systems with lower grain sizes. In the

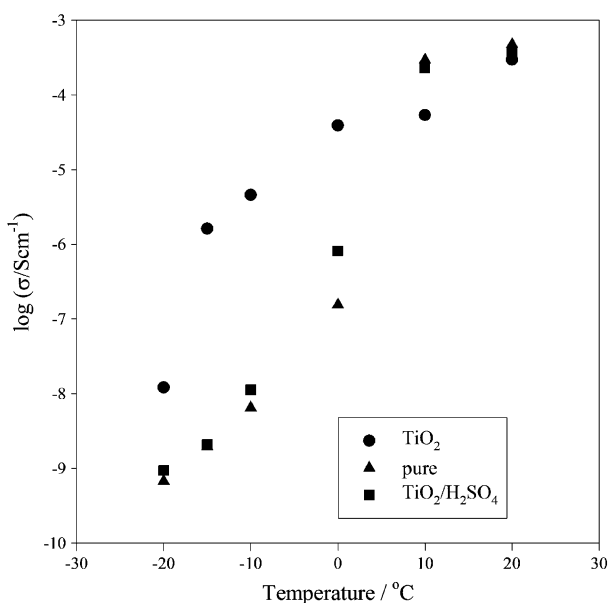


Fig. 2. Ionic conductivity of PEODME–(1 mol kg^{-1}) LiTFSI without and with 10 mass% of TiO_2 or $\text{TiO}_2/\text{H}_2\text{SO}_4$ composite polymeric electrolytes measured at low temperature.

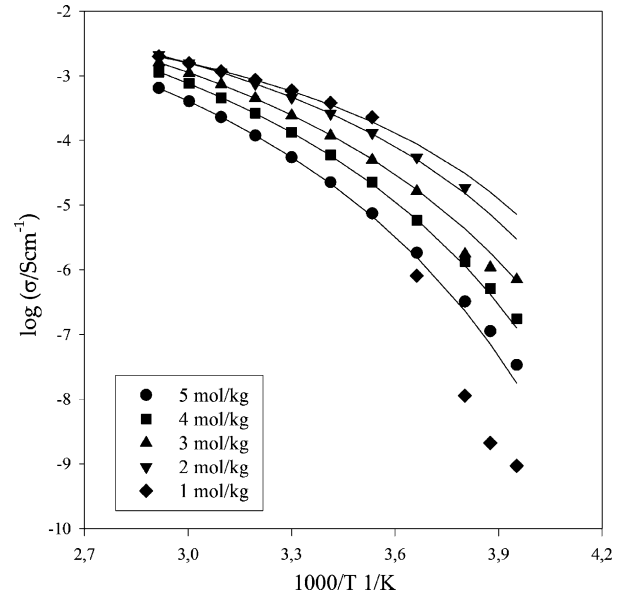


Fig. 3. Temperature dependence of ionic conductivity for PEODME–LiTFSI with 10 mass% of $\text{TiO}_2/\text{H}_2\text{SO}_4$ composite polymeric electrolytes with VTF fitting for different salt concentrations.

case of our studies the melting temperatures and heats of melting for both composite electrolytes are very similar. Therefore, higher conductivities observed for composites with nanofillers could be explained by the steric hindrance of the large surface modified fillers.

Fig. 3 presents typical temperature dependence of ionic conductivity for composite polymeric electrolytes for different salt concentration. For salt concentrations higher than 2 mol kg^{-1} electrolytes displayed Vogel–Tamman–Fulcher (VTF) behavior (VTF fits shown as solid lines). For system with 1 mol kg^{-1} of salt an abrupt decrease in conductivity is seen below $\sim 10^\circ\text{C}$.

The VTF expression is represented by

$$\sigma = A(T) - \frac{1}{2} \exp \left[-\frac{E}{R}(T - T_0) \right]$$

where A is the pre-exponential factor, which is related to the number of charge carriers, E the pseudo-activation energy of ion transport, R the gas constant ($8.314\text{ J K}^{-1}\text{ mol}^{-1}$) and T_0 is the equilibrium glass transition temperature. The value of T_0 used was 50 K below the glass transition temperature (T_g) obtained from DSC experiments.

Table 1 reports the results of the VTF fit. The calculated values of pre-exponential factor A and pseudo-activation energy E , decreases with the decrease of salt concentration for every systems. The only exception is the sample containing 2 mol kg^{-1} of the lithium salt and nanosize TiO_2 filler.

Table 2 presents glass transition temperature (T_g) and melting point (T_m) with heat of phase transition (Q_w) determined by DSC measurements. Generally, T_g increases with the increase of the salt concentration for all systems studied. Composite electrolytes without filler and with pure TiO_2 have the same T_g value for most salt concentrations. However for polymer electrolytes containing 5, 4 or 3 mol kg^{-1} LiTFSI, a decrease in T_g upon addition of modified TiO_2 was observed. Melting

Table 1
VTF parameters for PEO/DME–LiTFSI without or with different filler

Conc. salt (mol kg ⁻¹)	Filler (10 mass%)	A (S cm ⁻¹ K ^{1/2})	E (kJ mol ⁻¹)	T ₀ (K)
5	–	14.10	8.18	196
4	–	12.41	7.46	195
3	–	4.11	5.48	204
2	–	1.59	4.95	197
1	–	1.08	3.53	204
5	TiO ₂	8.00	7.94	196
4	TiO ₂	3.26	5.74	211
3	TiO ₂	0.63	3.92	219
2	TiO ₂	3.84	6.13	184
1	TiO ₂	0.32	2.89	205
5	TiO ₂ /H ₂ SO ₄	10.4	8.27	196
4	TiO ₂ /H ₂ SO ₄	8.66	8.24	195
3	TiO ₂ /H ₂ SO ₄	6.27	6.71	192
2	TiO ₂ /H ₂ SO ₄	2.48	4.99	198
1	TiO ₂ /H ₂ SO ₄	0.97	3.83	202

point (T_m) was observed only for the sample with the lowest salt concentration (1 mol kg⁻¹). It means that polymer electrolytes of higher salt concentration, without and with filler are completely amorphous. For system with 1 mol kg⁻¹ LiTFSI addition of the fillers decreases T_m in following sequence: filler free >10 wt% TiO₂ > 10 wt% TiO₂/H₂SO₄. The same sequence was observed for the heat of phase transition, assumed as a measure of the polymer crystallinity. Zhou and Fedkiw [3] observed slight increase in T_g and the same value of T_m upon addition of filler in all PEO/DME with LiTFSI (O/Li 1:20) systems studied. He interpreted this increase as a reduction in flexibility of polymer segments. Lewis-acid centers (–OH groups) on the filler surface interact with Lewis-base centers of the polymer, thus forming polymers-filler complex. We observed the opposite situation. Super acid (SO₄²⁻) groups in our filler do not change T_g in polymer electrolytes with 1 mol kg⁻¹ LiTFSI (which correspond O/Li 1:20). Addition of the filler decreases T_m compare to polymer electrolyte without the filler. The same effect was observed by Xi et al. [13] for nanocomposite polymer electrolyte based on PEO–LiClO₄ and solid super acid sulphated-zirconia.

FT-IR spectroscopy of composite electrolyte proves interactions between polymer chain, lithium salt and filler. In our spectra, peaks characteristic for ion–ion and ion–polymer interactions for composite polymer electrolytes were observed. Following the literature review follows the bond shift of C–O–C stretch mode with max around 1100 cm⁻¹ might be employed as an indicator of the Li⁺–polymer interaction. With an increase

Table 2
Glass transition temperature (T_g) and melting point (T_m) with heat of phase transition (Q_w) determined by DSC measurements

Conc. salt (mol kg ⁻¹)	Pure		TiO ₂		TiO ₂ /H ₂ SO ₄	
	T_g (K)	T_m (K), Q_w (J g ⁻¹)	T_g (K)	T_m (K), Q_w (J g ⁻¹)	T_g (K)	T_m (K), Q_w (J g ⁻¹)
5	233	–	233	–	227	–
4	224	–	224	–	221	–
3	218	–	219	–	216	–
2	208	–	210	–	210	–
1	203	279, 47.2	205	276, 36.6	203	272, 30.4

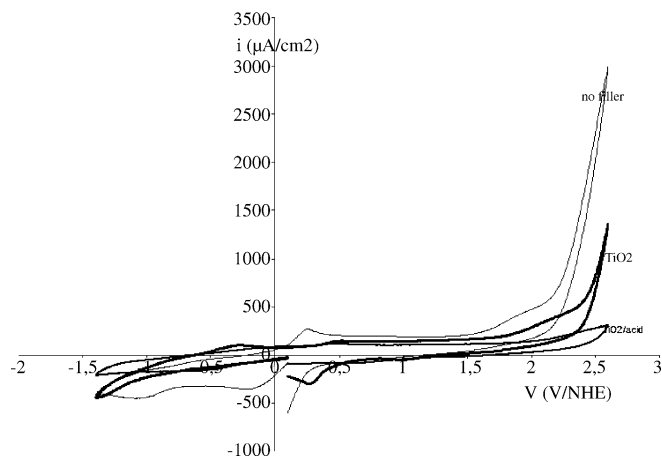


Fig. 4. Comparison of voltammetric curves for given electrolytes scan rate 50 mV s⁻¹.

in the salt concentration, the maximum of the C–O–C stretch is shifted to lower wavenumbers. No significant change in C–O–C peak position is observed in the presence of filler.

We have identified five characteristic peaks representing ion–ion interactions of TFSI⁻ for polymer electrolyte studied. Three peaks between 800 and 700 cm⁻¹ are identified as follows: 787–790 cm⁻¹ for the combination of C–S and S–N stretching, 761–763 cm⁻¹ as for the combination of C–S and C–F stretching and 740 cm⁻¹ for S–N stretching. Symmetric CF₃ stretching mode is assigned to 1195 cm⁻¹ and asymmetric SO₂ stretching mode is assigned to 1355 cm⁻¹ with a shoulder small peak at 1333 cm⁻¹ in the composite electrolyte based on PEO/DME–LiTFSI. In terms of ion–ion interactions we found no band shift for any peak upon addition of fillers.

Electrochemical stability of the electrolytes has been confirmed in amperometric tests (Fig. 4). In the potential range (up to 4 V) versus lithium electrode no oxidation–reduction phenomena occurred and the current density values did not exceed 0.1 mA cm⁻².

Preliminary studies of Li/polymer electrolyte interface showed that the addition of acidic filler influences the resistance of the electrolyte–electrode interface. Upon addition of TiO₂/H₂SO₄ the overall impedance of Li/electrolyte/Li cells grows much slower with time (Fig. 5). An equivalent circuit of parallel R–CPE (resistance-constant phase element) elements connected in series (bulk conductivity at high frequencies as R_{HF}||CPE_{HF}, interface layer at middle frequencies as R_{MF}||CPE_{MF}, charge transfer at low frequencies as

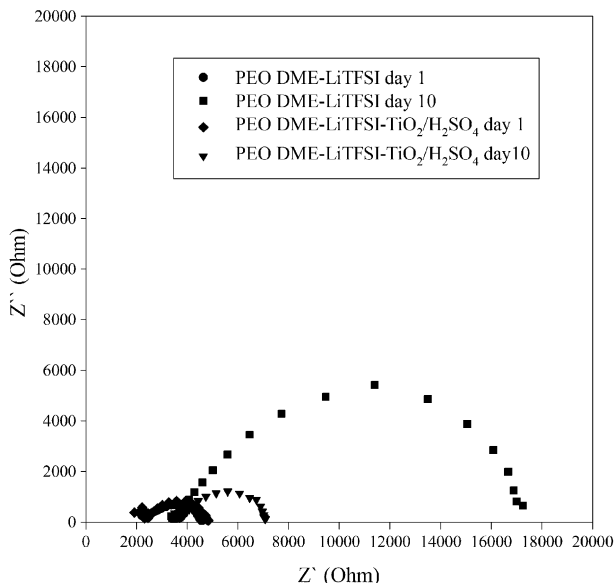


Fig. 5. Impedance spectra of Li–electrolyte–Li cell changes with time.

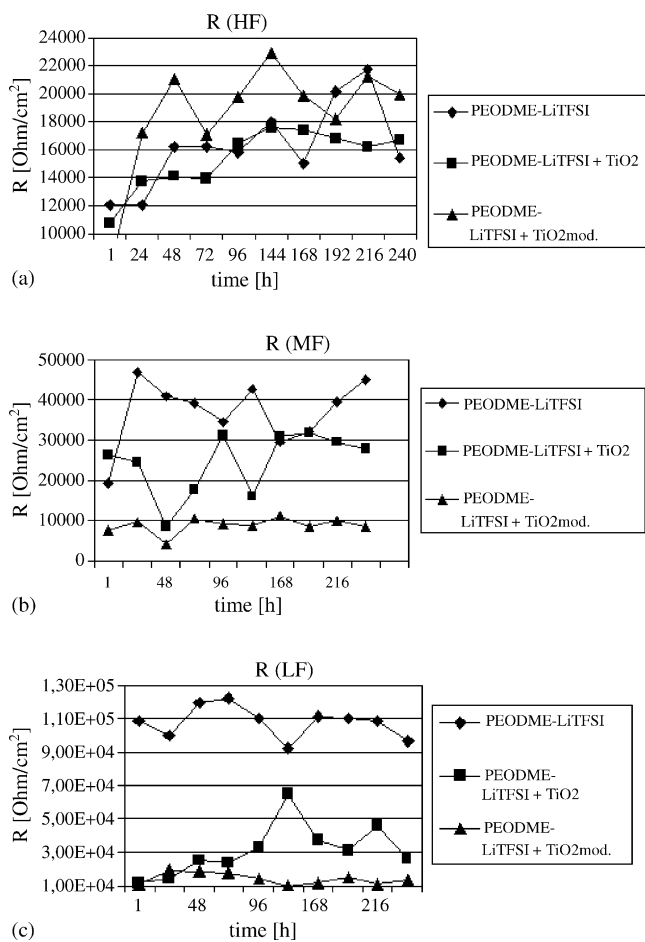


Fig. 6. Changes of R with time for parallel R -CPE elements: (a) bulk conductivity at high frequencies, (b) interface layer at middle frequencies and (c) charge transfer at low frequencies.

$R_{LF}||CPE_{LF}$) had been postulated and verified in our previous works [12,14] for high- and low-molecular weight poly(ethylene oxide) electrolytes. Similarity of experimental technique and preparation of samples allows us to apply it to analyse current impedance spectra.

Fig. 6a–c shows time changes of the bulk electrolyte resistance (Fig. 6a), electrode–electrolyte interfacial layer resistance (Fig. 6b) and charge transfer resistance (Fig. 6c). Bulk electrolyte resistance measured for three electrolytes studied generally, slightly increases with time. The values are rather scattered in time. Generally the bulk resistances for composite electrolytes with unmodified nanosize TiO_2 are the lowest and those obtained for composite systems with surface modified TiO_2 are the highest. The differences are within 30–40%.

More pronounced differences are found when analyzing time evolution of charge transfer and interfacial layers resistances. Charge transfer resistances obtained for composite systems are about an order of magnitude lower than for PEODME–LiTFSI electrolyte. The lowest and most stable in time values were measured for composites with surface modified TiO_2 . Interfacial layer resistances are the lowest and most stable for the same electrolytes. Resistances obtained for the other composite systems are slightly lower than for PEODME–LiTFSI electrolyte.

From the results presented in Fig. 6 it can be concluded that the addition of TiO_2 fillers results in the suppression of growth of interfacial electrode–electrolyte layers. Most probably acid centers of the fillers can create pathways for lithium cation thus making their transport to and from the electrode easier and decreasing the charge transfer and interfacial resistances.

4. Conclusions

Addition of filler show similar effect on conductivity in all concentration on salts and all temperatures studied. We can observe the difference only for system with 1 mol kg^{-1} salt in temperatures lower than 10°C . The highest conductivity has been measured for samples with pure unmodified TiO_2 .

The temperature dependence of σ can be described with the Vogel, Tamman and Fulcher equation. The calculated values of pre-exponential factor— A , pseudo-activation energies— E , increase with an increase in the salt concentration. The same trend was observed for changes in T_g .

Preliminary results of electrochemical studies indicate some stabilization of the interface and lowering of the overall resistance of lithium electrodes. In particular,

- conductivity phenomena stay uninfluenced by the additives during prolonged contact of lithium electrode with the electrolyte— R_{HF} ;
- interfacial resistance and charge transfer resistance grow slower with time or are almost stable in samples containing acidic filler— R_{MF} and R_{LF} .

Acknowledgement

This work was carried out in the frame of the VIth European Framework NOE “Alistore”.

References

- [1] F.M. Gray, *Solid Polymer Electrolyte—Fundamentals and Technological Applications*, VCH, New York, 1991.
- [2] B. Scrosati (Ed.), *Applications of Electroactive Polymers*, Chapman and Hall, London, 1993.
- [3] J. Zhou, P.S. Fedkiw, *Solid State Ionics* 166 (2004) 275–293.
- [4] M. Armand, W. Gorecki, R. Andreani, in: B. Scrosati (Ed.), *Proceedings of the Second International Symposium on Polymer Electrolytes*, Sienna, Italy, 1989, Elsevier, London, 1990, p. 4471.
- [5] L. Edman, A. Ferry, M.M. Doeff, *J. Mater. Res.* 15 (2000) 1950–1954.
- [6] M. Marcinek, A. Bac, P. Lipka, A. Zalewska, G. Żukowska, R. Borkowska, W. Wieczorek, *J. Phys. Chem. B* 104 (2000) 11088–11093.
- [7] F. Croce, R. Curini, A. Martinello, L. Persi, F. Ronci, B. Scrosati, R. Caminiti, *J. Phys. Chem. B* 103 (1999) 10632–10638.
- [8] F. Corce, G.B. Appetechi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456.
- [9] W. Wieczorek, A. Zalewska, D. Raducha, Z. Florjańczyk, J.R. Stevens, *J. Phys. Chem. B* 102 (1998) 352–360.
- [10] M. Marczewski, A. Jakubiak, H. Marczewska, A. Frydrych, M. Gontarz, A. Sniegula, *Phys. Chem. Chem. Phys.* 6 (2004) 2513–2522.
- [11] A. Bac, M. Ciosek, M. Bukat, M. Marczewski, H. Marczewska, W. Wieczorek, *J. Power Sources* 159 (2006) 405–411.
- [12] R. Borkowska, A. Reda, A. Zalewska, W. Wieczorek, *Electrochim. Acta* 46 (2001) 1737–1746.
- [13] J. Xi, X. Qiu, S. Zheng, X. Tang, *Polymer* 46 (2005) 5702–5706.
- [14] R. Borkowska, J. Laskowski, J. Płocharski, J. Przyłuski, W. Wieczorek, *J. Appl. Electrochem.* 23 (1993) 991–995.