Characterization of polymer electrolytes based on poly(dimethyl siloxane-co-ethylene oxide)

C. Polo Fonseca[*], S. Neves

Laboratório de Caracterização e Aplicação de Materiais (LCAM), Universidade São Francisco, Campus Itatiba, 13251-900 Itatiba, SP, Brazil

Abstract

The usefulness of poly(dimethyl siloxane-co-ethylene oxide) (P(DMS-co-EO)) copolymer as an ion conducting matrix was investigated. The electrochemical properties were studied by electrochemical impedance spectroscopy and cyclic voltammetry. The glass transition temperature (T_g) and degree of crystallization as a function of salt concentration were examined by differential scanning calorimetry. Ionic conductivities as high as 2.6×10^{-4} S cm^{-1} were determined at 25 °C for copolymers films with 5 wt.% LiClO$_4$. These same films had an electrochemical stability window of 5 V. The pseudo-activation energy as a function of salt concentration was obtained using the Vogel–Tamman–Fulcher (VTF) equation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Ionic conductivity; Copolymer; Electrochemical stability window

1. Introduction

Solid polymer electrolytes (SPEs) have been proposed as a substitute for the liquid electrolyte in electrochemical devices and one widely used in lithium batteries. Current research for a suitable SPE is aimed mainly at the development of high energy-density rechargeable batteries which can be used in cellular phones, notebook computers, electrochromic displays and electric vehicles.

The SPE is formed by the incorporation of lithium salt into polymer matrices. These materials show a lower ionic conductivity than liquid electrolytes, but are less reactive with lithium and, thus, increasing the safety of the batteries. The SPE can be used as the electrolyte, as a separator or both. The ability of SPE to form thin flexible, transparent films increasing the design possibilities for thin batteries.

The initial work with SPE was done using a linear poly(ethylene oxide) (PEO) with lithium salts (LiClO$_4$ and LiN(CF$_3$SO$_2$)$_2$) dissolved in the polymeric matrix [1]. PEO is a polycrystalline material with good mechanical properties but a low ionic conductivity (10^{-8} S cm^{-1}) at room temperature [2].

Amorphous PEO salt complexes show superior ionic conductivity when compared to crystalline PEO salt complexes, probably because of the segmental motion of the polymeric chain during ion transport. The glass transition temperature (T_g) of amorphous PEO is lower than that of crystalline PEO and consequently, its ionic conductivity is higher. The presence of the crystalline phase reduces the ionic conductivity at room temperature [1,2].

Several studies have investigated the possibility of decreasing of polymer crystallinity and this has lead to formation of new polymer electrolyte classes. Such combinations include:

1. *Blends*—in devices where high pressure is applied, amorphous polymer electrolytes are not always suitable because they are generally susceptible to creep, even at low pressure. Therefore, for electrochemical applications where mechanical stability is also important, copolymers of PEO [3–5] and PEO blended with macromolecules or inorganic supports are used as SPE. Both the PEO copolymer and blend and copolymer of PEO inhibits the crystallinity of PEO [5,6].
2. *Hybrids*—recent reports [7–9] have described inorganic network growth in solutions containing organic polymers, such as poly(vinyl alcohol), poly(acrylic acid), poly-(methyl methacrylate), poly(vinyl pyrrolidone), poly-(ethylene oxide) and NAFION®.
3. *Gels* represent a type of polymer electrolyte in which the liquid electrolyte is immobilized by incorporation into a polymer matrix. In such systems, ionic conductivity

* Corresponding author. Tel.: +55-11-4534-8071;
fax: +55-11-4524-1933.
E-mail address: cfonseca@usf.com.br (C.P. Fonseca).

occurs as much in the polymeric phase as in the solution phase. Cross-linking, gelification or casting can produce liquid immobilization. Cross-linking is usually carried done with ultraviolet or gamma ray irradiation. An ionic conductivity as high as 10^{-3} S cm^{-1} at 20 °C has been obtained [10–14].

4. *Plasticized polymer electrolyte*—through the addition of a liquid plasticizer such as propylene carbonate, an improvement in the ionic conductivity of about 10^{-4} S cm^{-1} has been observed. However, to obtain this result, a high amount of plasticizer was necessary and this adversely affected the mechanical stability of the PEO [15–17].

Properties such as a high ionic conductivity, a low T_g, a large number of charge carriers and a wide electrochemical stability window are necessary for the good operation of an electrochemical device.

In this work, we report an investigation of the poly-(dimethyl siloxane-co-ethylene oxide) (P(DMS-co-EO)) system, in the presence of several concentrations of LiClO$_4$ salt. The ionic conductivity as a function of salt concentration, activation energy, electrochemical stability window, absorption spectra and thermal properties of this system were analyzed.

2. Experimental

The P(DMS-co-EO) was synthesized by a polycondensation reaction of dimethyldichlorosilane with monoethylene glycol [3]. The P(DMS-co-EO)/LiClO$_4$ complexes were prepared by mixing the polymer and salt in tetrahydrofuran (THF). The solution was dried in vacuum for 48 h. The final salt concentrations were 2.5, 5.0, 10.0, 15.0 and 20.0 wt.% of LiClO$_4$, respectively.

Thermal analysis was done using a differential scanning calorimeter (NETZSCH DSC 204) under a nitrogen atmosphere, at a heating rate of 10 °C min^{-1}. The temperature routine involved was the following:

1. Heating from room temperature to 150 °C to eliminate the *thermal history* of the sample.
2. Cooling from 150 to −100 °C.
3. Second heating to 200 °C.

All DSC experiments were done in duplicate and the thermograms shown in the next section refer to the second heating.

The ionic conductivity was measured by electrochemical spectroscopy impedance using an AUTOLAB-PGSTAT30 FRA. An ac amplitude of 10 mV was applied and the data were collected in the frequency range 1–10^5 Hz. To obtain the ionic conductivity as a function of temperature, the experiments were done using a thermally stabilized electrochemical cell. The temperature range analyzed was from −30 to 80 °C, at a heating rate of 3.0 °C min^{-1}. The samples

were sandwiched between two polished stainless steel (SS) disks (area of 1.0 cm^2) which acted as ion-blocking electrode. A Teflon spacer 0.05 mm thick was used to prevent short-circuits and to maintain a fixed thickness in the samples during measurements at high temperature and under pressure.

The Li/polymer electrolyte interface behavior was analyzed using two lithium electrodes obtained by pressing lithium foils on the surface of the SS disks (1 cm^2). The Li/P(DMS-co-EO)/Li cell was stored for 360 h at a constant temperature (23 °C) and the impedance spectra were measured at various time intervals.

The electrochemical stability window was evaluated by cyclic voltammetry at a scan rate of 10 mV s^{-1} using an Li/polymer electrolyte/SS cell, where the same lithium metal was used as the counter and reference electrodes. The preparation of the cell, and the ionic conductivity and electrochemical stability window measurements were done in a dry box with an argon atmosphere.

The UV–VIS measurements of P(DMS-co-EO)/LiClO$_4$ films with different salt concentrations were done using an HP 8453 spectrophotometer. The background signals from the ITO glass substrate were considered as 0% absorbance.

3. Results and discussion

The DSC thermograms of the polymer electrolytes are shown in Fig. 1. The material showed a crystalline phase with an endothermic peak at −7.2 °C that was probably related to the melting point of DMS [18]. With the increase in salt concentration this endothermic peak disappeared. The P(DMS-co-EO) with 5 wt.% LiClO$_4$ gave no thermal response at temperatures above the T_g, showing a amorphous material characteristics. The crystallinity of P(DMS-co-EO) was suppressed through increased cross-linking in the chains. The decrease in the melting temperature (T_m) from
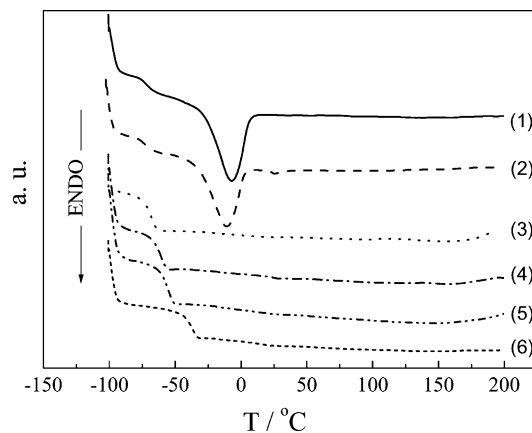

Fig. 1. Differential scanning calorimetry curves for P(DMS-co-EO) samples at different salt concentrations (C): (1) $C = 0$, (2) $C = 2.5$, (3) $C = 5.0$, (4) $C = 10.0$, (5) $C = 15.0$ and (6) $C = 20.0$ wt.% LiClO$_4$.
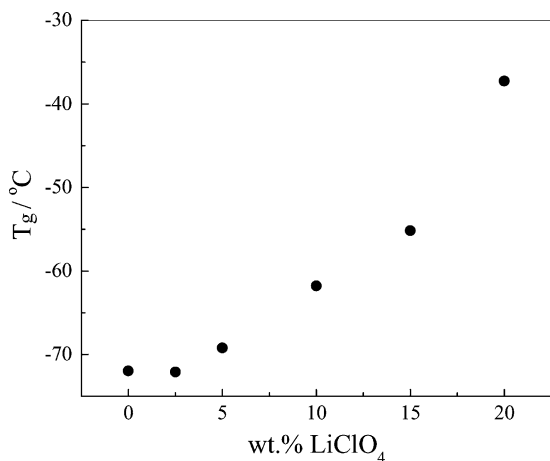
Fig. 2. Variation in the T_g as a function of salt concentration.

Fig. 4. Ionic conductivity as a function of salt concentration at room temperature.

−7.3 to −11.2 °C with salt addition was probably related to the cross-linking process [19,20].

A polymer with a low T_g is a suitable candidate for combination with salts to form polymeric electrolytes. Below the T_g, physical properties such as viscosity, diffusion and conduction become less sensitive to temperature, whereas, above the T_g, the segmental motion of the polymeric chain increases. The T_g values rose with increasing values of the salt concentration (Fig. 2) and this was indicative of a decrease in the segmental motion of the polymeric chain.

The conductivity was determined by an ac impedance analysis. Fig. 3 shows the impedance plots of P(DMS-co-EO)/LiClO$_4$ with 20 wt.% LiClO$_4$ at different temperatures. At low temperatures, a semi-circle was observed that was related to the impedance of the polymer electrolyte (Z). The bulk resistance was obtained from the impedance spectra at the point where the arc intercepted the real part in the low frequency region. With the increase in temperature, this semi-circle tended to disappear and shifted to a lower resistance value, thereby, increasing the ionic conductivity.
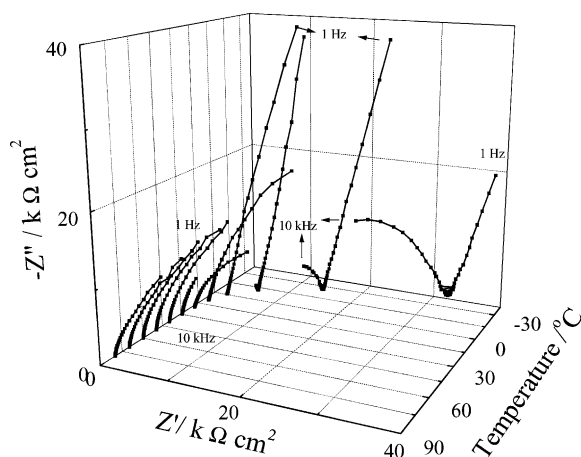

Fig. 3. An ac impedance spectrum of the SS/P(DMS-EO)/SS system at different temperatures. The LiClO$_4$ salt concentration was 20 wt.%
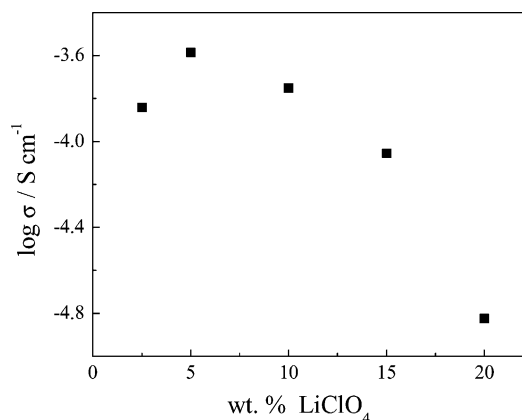
The conductivity value was calculated using the equation:

$$\sigma = \frac{\ell(\text{cm})}{Z(\Omega)A(\text{cm}^2)} \tag{1}$$

where ℓ is the thickness of the polymer electrolyte (the same thickness as the Teflon spacer, 0.05 mm), Z the impedance of the electrolyte estimated from the Nyquist plot and A the stainless steel electrode area covered by the polymer electrolyte (1.0 cm^2).

The low frequency region of the impedance spectrum contained information on the electrode/electrolyte interface. The deviation of the vertical line may be indicative of surface adsorption or an unexpected electrochemical reaction at the interface [21].

Fig. 4 shows how variations in the salt concentration variation in the polymeric matrix influenced the ionic conductivity of the salt polymer complex at room temperature. A typical ionic conductivity curve was observed, with a maximum at 5 wt.% LiClO$_4$. These experiments were done at room temperature and the maximum ionic conductivity value was 2.6×10^{-4} S cm^{-1}. This maximum reflected the increase in the concentration of charge carriers when salt was added into the polymer. The decrease of ionic conductivity after the maximum is attributed to three related phenomena:

1. An increase in the macromolecular rigidity of the amorphous phase caused by the presence of a high salt concentration, which acted as a reticulate agent in the polymeric matrix. The increase in T_g (Fig. 2) for salt concentrations greater than 5 wt.% LiClO$_4$ corresponded precisely to the ratio in which ionic conductivity started to decrease.
2. The non-linear increase in charge carrier number as a function of salt concentration, which favored the appearance of ion pairs.
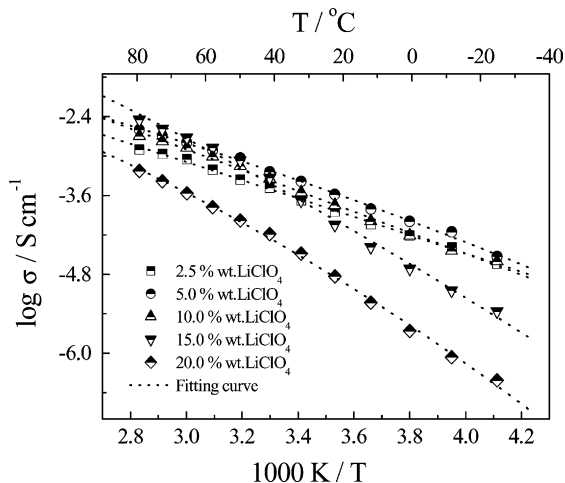3. The appearance of a crystalline phase composed of salt–polymer complexes.

Fig. 5. Arrhenius plot: variation in ionic conductivity as a function of the salt concentration and temperature.

Fig. 7. Cyclic voltammogram for a Li/P(DMS-co-EO) + 5 wt.% LiClO$_4$/SS system. Scan rate = 5 mV s^{-1}.

Fig. 5 shows the variation in the ionic conductivity of salt–polymer complexes as a function of temperature (Arrhenius plots). According to the free volume theory, the ionic transport mechanism in the polymer electrolyte resulted from the segmental motions. This process promoted ion movement through the formation and destruction of the coordination sphere of the solvated ion, thereby, creating a space (free volume) into which the ion could diffuse under the influence of the electrical field [2]. The ion was transported by the semi-random motion of the short polymer segments and at temperatures below the ideal glass transition temperature (T_0), the free volume was assumed to vanish. The motion of ions and polymer segments at temperatures above T_0 was facilitated by the creation of a free volume.

The Vogel–Tamman–Fulcher (VTF) Eq. (2) fitted these curves more accurately:

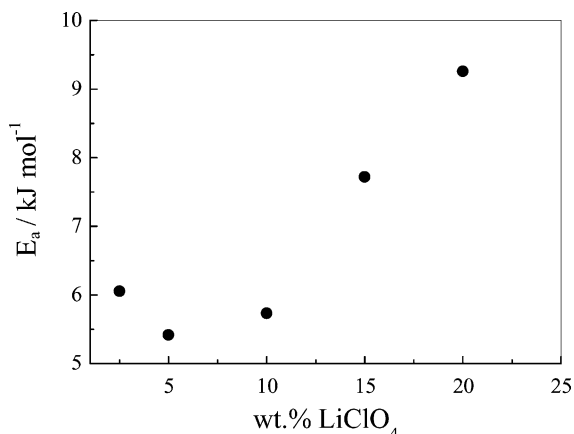$$\sigma = \sigma_0 \; \exp\left(-\frac{B}{T - T_0}\right) \qquad (2)$$

where σ_0 is related to the effective number of charge carriers in the system and B is the pseudo-activation energy necessary for the redistribution of the free volume.

The pseudo-activation energies of the polymer electrolyte (Fig. 6) were obtained by fitting the data in Fig. 5 using the VTF equation. A minimum in the pseudo-activation energy was observed at 5 wt.% LiClO$_4$. At high salt concentrations, there was an increase in the pseudo-activation energy. This behavior may be explained by considering that the segmental motion of P(DMS-co-EO) decreased with increasing salt concentration (Fig. 2), and that high energies were needed to promote such segmental motion. These values were of the same magnitude as those reported for the PEO system, indicating that both show a similar ionic conduction mechanism [22].

A knowledge of the electrochemical stability window is essential for the successful performance of any device, especially energy storage devices. Armand et al. [23] did
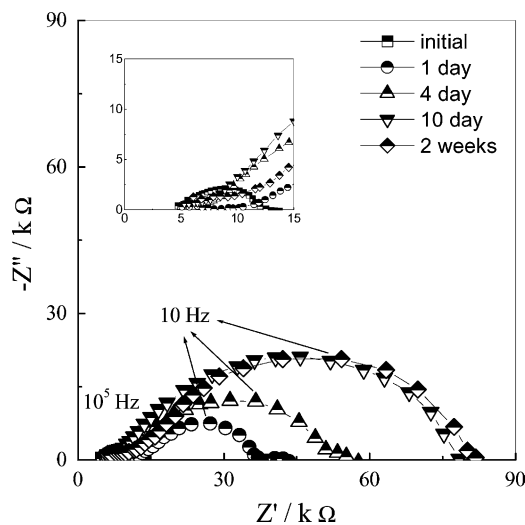

Fig. 6. Pseudo-activation energy as a function of the salt concentration.

Fig. 8. The ac impedance spectrum of an Li/P(DMS-co-EO) + 5 wt.% LiClO$_4$/Li system as a function of time at room temperature.
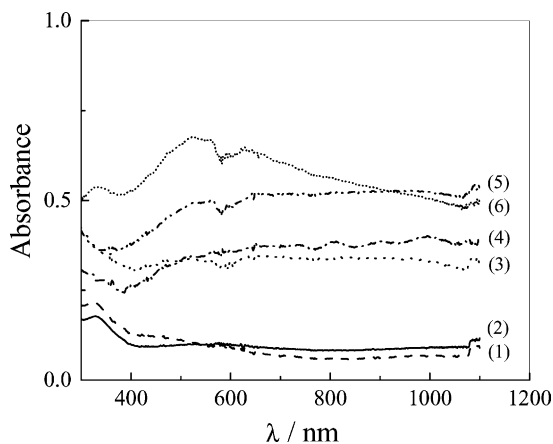
Fig. 9. Absorbance spectrum of an ITO/P(DMS-co-EO) system at different salt concentrations (*C*): (1) *C* = 0, (2) *C* = 2.5, (3) *C* = 5.0, (4) *C* = 10.0, (5) *C* = 15.0 and (6) *C* = 20.0 wt.% LiClO$_4$.

the first studies on the electrochemical stability window of a solid polymeric electrolyte. Fig. 7 shows the cyclic voltammetry for the SS/P(DMS-co-EO) + LiClO$_4$/Li system with 5 wt.% LiClO$_4$ at room temperature. The salt that was polymer complex showed an electrochemical stability window of approximately 5 V, limited cathodically by pseudo-reversible lithium deposition. The pseudo-plateau between 1 and 0 V was attributed to salt reduction. The anodic limit has been related to anion oxidation followed by possible polymeric degradation [21,24].

Fig. 8 shows the Li/polymer interface behavior at different times under open circuit potential conditions at room temperature. At a high frequency, the first interception of data, at high frequency was related to bulk resistance. With increasing time, no changes were observed in the bulk resistance values at any of the salt concentrations, thus, indicating the stability of the polymer electrolyte (inset in Fig. 8). A semi-circle in the medium frequency range represented the interfacial charge-transfer resistance (R_{ict}). This semi-circle increased quickly during the first 10 days and thereafter stabilized. This increase has been attributed to the formation of a passive film caused by the reactivity of the electrode/polymer electrolyte interface [25,26].

Fig. 9 illustrates the UV–VIS absorption spectrum for P(DMS-co-EO)/LiClO$_4$. There was no significant absorption in the visible region at any of the salt concentrations. This observation is important for electrochromic applications.

4. Conclusions

P(DMS-co-EO)/LiClO$_4$ electrolyte is a transparent material in the visible region. The maximum ionic conductivity determined was 2.6×10^{-4} S cm^{-1} for the salt–polymer complex with 5 wt.% LiClO$_4$ at room temperature. A high conductivity was obtained, even at low temperatures ($T = -30$ °C, $\sigma_{5\,wt.\%\,LiClO_4} = 3.0 \times 10^{-5}$ S cm^{-1}). The wide electrochemical stability window of approximately 5 V,

confirmed that P(DMS-co-EO)/LiClO$_4$ electrolyte had the most of the electrochemical properties necessary for use in electrochemical devices.

Acknowledgements

References

[1] M.B. Armand, J.M. Chabagno, M. Duclot, in: P. Vashista, J.M. Mundy, G.K. Sherroy (Eds.), Fast-Ion Transport in Solids, North-Holland, Amsterdam, 1979.

[2] P.G. Bruce, C.A. Vincent, J. Chem. Soc., Faraday Trans. 89 (1993) 3187.

[3] K. Nagaoka, H. Nasure, I. Shinohara, J. Polym. Sci., Polym. Lett. 22 (1984) 659.

[4] R.A. Zoppi, C. Polo Fonseca, M.-A. De Paoli, S.P. Nunes, Solid State Ionics 91 (1996) 123.

[5] A. Bakker, J. Lindgren, K. Hermansson, Polymer 37 (1996) 1871.

[6] J. Sun, D.R. Macfarlane, M. Forsyth, Electrochim. Acta 40 (1995) 2301.

[7] R.A. Zoppi, C. Polo Fonseca, M.-A. De Paoli, S.P. Nunes, Acta Polym. 48 (1997) 131.

[8] D.A. Loy, K.J. Shea, Chem. Rev. 95 (1995) 1431.

[9] U. Schubert, N. Husing, A. Lorenz, Chem. Mater. 7 (1995) 2010.

[10] M. Alamgir, K.M. Abraham, Room temperature polymer electrolytes, in: G. Pistoia (Ed.), Lithium Batteries, Elsevier, Amsterdam 1983 (Chapter 3).

[11] Z. Florjanczyk, W. Bzducha, N. Langwald, J.R. Dygas, F. Krok, B. Misztal-Faraj, Electrochim. Acta 45 (2000) 3563.

[12] B.B. Owens, P.M. Skarstad, D.F. Untereker, Solid-electrolytes cells, in: D. Linden (Ed.), Handbook of Batteries, 2nd Edition, McGraw-Hill, New York, 1995 (Chapter 15).

[13] H. Akashi, K. Sekai, K.-I. Tanaka, Electrochim. Acta 43 (1998) 1193.

[14] G.G. Kumar, N. Munichandraiah, Electrochim. Acta 44 (1999) 2663.

[15] D.G.H. Ballard, P. Chesire, T.S. Mann, J.E. Przeworshi, Macromolecules 23 (1990) 1256.

[16] M. Ishikawa, M. Morita, M. Ilhara, Y. Matsuda, J. Electrochem. Soc. 141 (1994) 1730.

[17] T.J. Benedict, S. Banumathi, A. Veluchamy, R. Gangadharan, A. Zulfihar, S. Rajendran, J. Power Sources 75 (1998) 171.

[18] J. Brandrup, E.H. Immergut (Eds.), Polymer Handbook, 2nd Edition, Wiley, New York, 1975, Chapter 3, p. 139.

[19] H.E. Bair, P.K. Gallagher, M. Jaffe, Y.P. Khana, J.J. Maurer, E.M. Pearce, R.B. Prime, D. Raucher, S.W. Shalaby, W.W. Wendlandt, B. Wunderlich, in: E.A. Turi (Ed.), Thermal Characterization of Polymeric Material, Academic Press, FL, 1981.

[20] J. Zimmerman, in: H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, J.I. Kroschwitz (Eds.), Encyclopedia of Polymer Science and Engineering, 2nd Edition, Vol. 11, Wiley, New York, 1998, p. 315.

[21] B. Scrosati, in: J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolytes Reviews-1, Wiley, New York, 1987.

[22] S. Takeoka, H. Ohno, E. Tsuchida, Polym. Adv. Technol. 4 (1993) 53.

[23] M. Armand, M.J. Duclot, P. Rigaud, Solid State Ionics 3/4 (1981) 429.

[24] J.S. Tonge, D.F. Shriver, The Electrochemistry of Novel Materials, VCH, New York, 1993 (Chapter 5).

[25] D. Fauteux, Solid State Ionics 17 (1985) 133.

[26] Z. Florjanczyk, W. Bzducha, N. Langwald, J.R. Dygas, F. Krok, B. Misztal-Faraj, Electrochim. Acta 45 (2000) 3563.