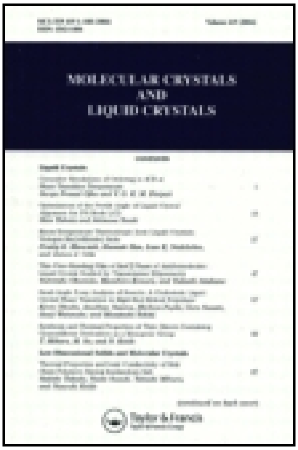


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A.C Impedance, X-ray Diffraction and DSC Investigation on Gelatin Based-Electrolyte with $LiClO_4$

Diogo F. Viera [a] , César O. Avellaneda [a] & Agnieszka Pawlicka [a]

[a] DFQ, IQSC - USP, Sao Carlos-SP, Brazil

Version of record first published: 31 Aug 2012.

To cite this article: Diogo F. Viera , César O. Avellaneda & Agnieszka Pawlicka (2008): A.C Impedance, X-ray Diffraction and DSC Investigation on Gelatin Based-Electrolyte with $LiClO_4$, Molecular Crystals and Liquid Crystals, 485:1, 843-852

To link to this article: http://dx.doi.org/10.1080/15421400801922304

Mol. Cryst. Liq. Cryst., Vol. 485, pp. 95/[843]–104/[852], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801922304

A.C Impedance, X-ray Diffraction and DSC Investigation on Gelatin Based-Electrolyte with $LiClO_4$

Diogo F. Viera, César O. Avellaneda, and Agnieszka Pawlicka
DFQ, IQSC – USP, Sao Carlos-SP, Brazil

Natural polymers are particularly interesting due to their richness in nature, very low cost and principally biodegradation properties. For these reasons different solid polymeric electrolytes (SPE) have been obtained using cellulose derivatives, starch, chitosan and rubber. This work presents the results of gelatin-based electrolyte, which were characterized by impedance spectroscopy, X-ray diffraction and thermal analysis. The ionic conductivity results obtained for these SPEs were 1.5×10^{-5} *S/cm and* 4.9×10^{-4} *S/cm at room temperature and 80°C, respectively. Temperature-dependence ionic conductivity measurements were taken to analyze the mechanism of ionic conduction in polymer electrolytes. Thermal analysis using differential scanning calorimetry (DSC) was performed in order to observe the change in transition temperature caused by the addition of salt to the electrolyte. Good conductivity results combined with transparency and good adhesion to the electrodes have shown that gelatin-based SPEs are very promising materials to be used as solid electrolytes in electrochromic devices.*

Keywords: conductivity and gelatin; solid electrolyte

INTRODUCTION

The interest in the study of polymer electrolyte systems is continually growing, due to the potential application of these materials to a great variety of electrochemical devices, such as high energy density batteries, fuel cells, sensors and electrochromic devices [1]. The development of a polymer system with high ionic conductivity is one of the main objectives in polymer research. Various approaches have been made to modify the structure of polymer electrolytes in order to

---

The authors are indebted to FAPESP and CNPq for the financial support given to this research.

Address correspondence to Agnieszka Pawlicka, DFQ, IQSC – USP, C.P. 780, Sao Carlos-SP, CEP 113560-970, Brazil. E-mail: agnieszka@iqsc.usp.br

improve their electrical and electrochemical properties [2]. These approaches include the use of crosslinking agents to form networks, blending polymers, block copolymers and addition of inert fillers with the polymer electrolytes [3–6].

On the other hand, in designing a novel polymer electrolyte, emphasis is placed on the increase of the amorphous phase content in the polymer, which provides fast ion motion while maintaining its mechanical stability [7]. However the addition of salt to the polymer matrix, which also improves ionic conductivity, can also increase the percentage of the crystallinity phase of the polymer.

Attention has been recently focused on natural polymers usually applied by cosmetic, pharmaceutical and food industry, due to of their biodegrability, low production cost and good physical and chemical properties. As examples, grafted hydroxyetlhycellulose (HEC), modified starch or natural rubber have been used to prepare electrolytes, which have achieved Li^+ ions conductivity values as high as 10^{-5} S/cm at room temperature. Small ECDs with good color/bleaching properties have also been already realized with these SPEs [8,9].

In the present work, gelatin-based polymer electrolytes were prepared and characterized. The characterization of the samples was performed by AC impedance spectroscopy in order to study the ionic conductivity of the polymer electrolytes. Thermal analysis using differential scanning calorimetry (DSC) was performed in order to observe the change in glass transition temperature caused by the lithium salt addition to the electrolyte. The structure of the electrolyte was studied by X-ray and the optical properties were analyzed using spectrophotometer measurements to emphasize that this material can be used in electrochromic devices.

EXPERIMENTAL

Solid Polymeric Electrolyte

The electrolyte was prepared according to the following procedure: 2 g of commercial uncolored gelatin (Oetker®) was dispersed in 15 mL of water and heated under magnetic stirring for a few minutes up to 50°C to complete dissolution. Then, 0.3 g of $LiClO_4$, 1.25 g of glycerol and 0.25 g of formaldehyde were added to this solution under stirring. This viscous solution was then cooled down to 30°C and poured on Petri plates to form transparent films.

Characterization Techniques

The structure of the film was examined by X-ray diffraction. The data were recorded using a Siemens D-5000 instrument with CuK_α radiation.

Differential scanning calorimetry measurements were obtained using Shimadzu DSC-50 equipment at a heating rate of 5 K/min under nitrogen atmosphere in the temperature range of 173–393 K.

The UV-Vis optical spectra of the electrolytes were recorded with an Agilent Spectrophotometer Instrument between 200 and 1100 nm.

Impedance spectroscopy measurements were used to determine the ionic conductivity and frequency behavior of the electrolyte. A 2 cm round and 0.5 mm thick piece of the electrolyte was pressed against two steel electrodes. The measurements were taken with an Autolab instrument equipped with an FRA2 module, applying a voltage of 5 mV rms amplitude in the frequency range $f = 10^6$ Hz to 10^1 Hz.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 shows typical X-ray diffraction patterns obtained for the gelatin-based electrolyte having different amounts of lithium salt. No crystalline peaks are observed and only a broad weak peak is seen at $2\theta \approx 22°$. The electrolytes are therefore X-ray amorphous with a weak partial crystalline structure.

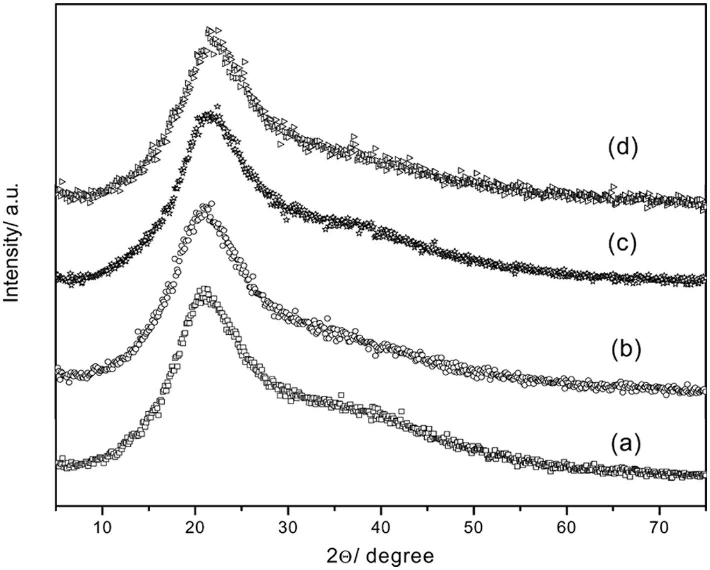
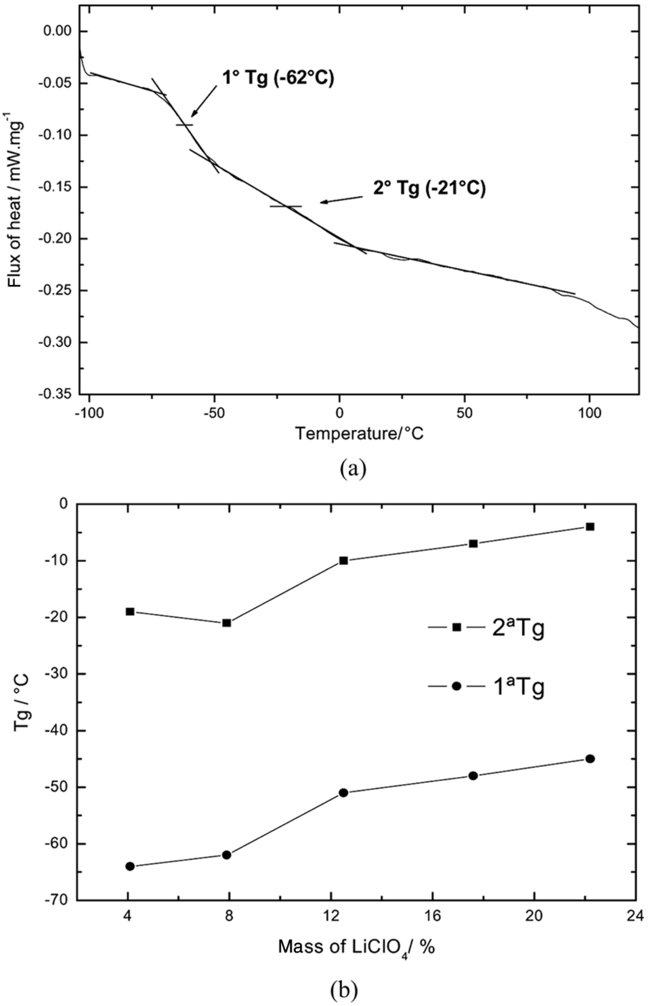


FIGURE 1 XRD pattern of gelatin electrolyte with different amounts of lithium salt: (a) 5.4%, (b) 7.9%, (c) 12.5% and (d) 22.2% of $LiClO_4$.

Thermal Analysis

Thermal analysis using differential scanning calorimeter (DSC) was performed in order to observe the change in the transition temperature caused by the addition of lithium salt. From Figure 2a, for the gelatin-based polymer electrolyte with 0.3 g of $LiClO_4$, two thermal transition temperatures can be observed in the temperature range studied. The Tg_1 occurs to lower temperatures and could be attributed



(a)

(b)

FIGURE 2 Thermal analysis of a gelatin-based electrolyte with 7.9 wt% of $LiClO_4$ (a) and the influence of $LiClO_4$ content on the Tgs values (b).

to the glycerol or to the movement of molecules and polymers side chains. The Tg_2 is related to the movement of the polymeric chains and to the ionic conductivity values, therefore it is the most important property for this wok [10].

Figure 2b shows the influence of $LiClO_4$ content on the Tgs values. It is possible to observe a decrease in the Tg_2 reaching a lower value that can be associated with the electrolyte with the highest conductivity and the lowest activation energy. After that, a significant increase in Tg_1 and Tg_2 with increasing $LiClO_4$ concentration is observed. This can be interpreted on the basis of chain flexibility, which is reflected by Tg. This increase in Tg may be attributed to the formation of ion pairs or ion clusters with increasing salt concentration. Similar results were also obtained by Silva *et al*. [11] and Ghiodelli *et al*. [12].

Optical Properties

Figure 3 shows the optical transmittance spectra for the three different gel electrolytes in the 200–1100 nm region. As the lithium content increases, there is a decrease in the optical transmittance due to a lower dissolution for higher lithium contents in the electrolyte producing non transparent films.

For the electrolyte containing 7.9 wt% of $LiClO_4$, almost zero transmission intensity can be observed in the 200–280 nm wavelength

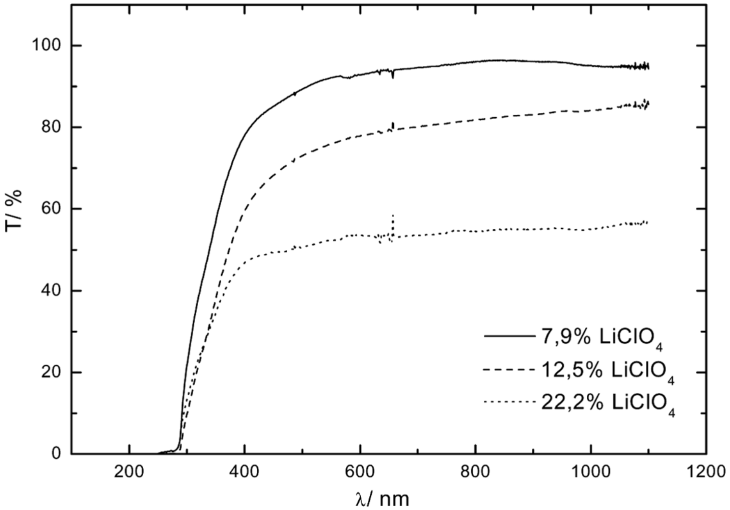


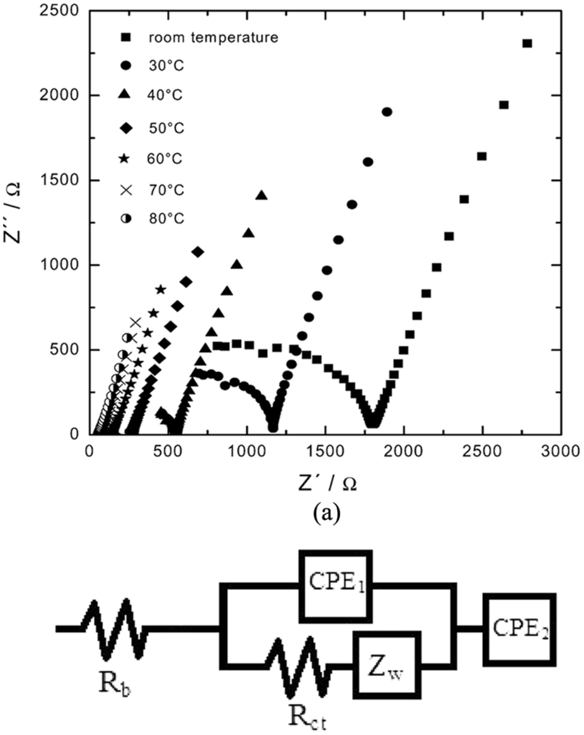
FIGURE 3 UV-Vis transmittance spectra of gelatin-based electrolytes.

range. Therefore the transmission intensity starts increasing at 280 nm until it reaches 88% at 550 nm after that the transmission is practically constant. This property makes the polymer electrolyte very attractive for use in electrochromic devices.

Impedance Analysis

Figure 4 shows the impedance plots for gelatin-based electrolytes at various temperatures. The bulk resistance values decrease with the increase in temperature.

The ionic conductivity values increase from 1.5×10^{-5} to $4.9 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ when the temperature increases from room temperature to 80°C, respectively, and the films are found to be mechanically stable. At higher temperatures, the thermal movement of polymer chain segments and the dissociation of salt would be improved



(a)

(b)

FIGURE 4 Complex impedance plots for the gelatin electrolyte measured at different temperatures (a) and equivalent circuit (b).

increasing the ionic conductivity. In the complex impedance plot (Fig. 4), the disappearance of a depressed semicircle at high frequency with the temperature reveals the absence of capacitive nature, i.e., a diffusion process. The interception of the semicircle with the real axis yields the electrolyte resistance (R_b). The values decrease with the increase in the sample temperature as the ionic mobility and the number of carrier ions with temperature increase [13].

The fitting of the impedance result with an equivalent circuit showed in Figure 4 is given in Figure 5, where R_b is the electrolyte resistance and CPE_1 is the constant phase element in parallel with the charge transfer (interfacial) resistance (R_{ct}) and Warburg element (Z_w, for diffusion) in series with the constant phase element (CPE_2). The CPE_1 and CPE_2 may be associated with the bulk electrolyte and the double layer capacitances, respectively.

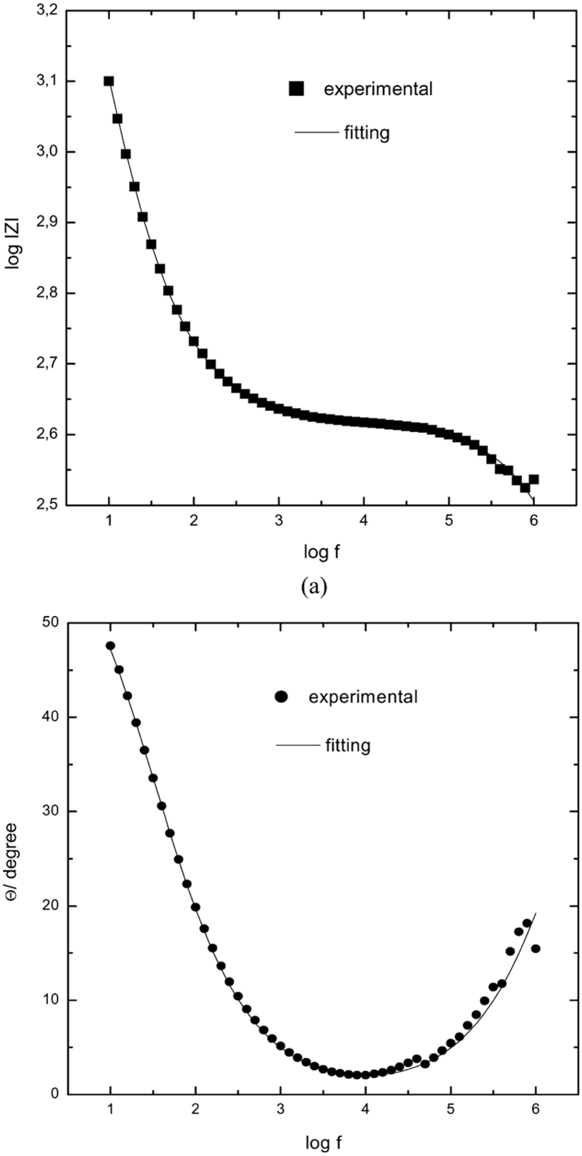
The impedance data for the films were fitted for the circuit showed in Figure 5 using Equivcrt software. Figure 5 shows that a good agreement between both experimental and impedance fitted data could be accomplished.

Conductivity Analysis

Figure 6 shows the room temperature ionic conductivities and activation energy variations of gelatin-based electrolytes as a function of lithium content. The activation energy for conduction decreased gradually with the increase in the $LiClO_4$ concentration until 7.9 wt% of $LiClO_4$, which is in agreement with the fact that the amount of ions in the polymer electrolyte increases by increasing the $LiClO_4$ concentration. Therefore the energy barrier to the lithium transport decreases, which would lead to a decrease in the activation energy [14]. From this value the activation energy starts to increase, as more energy is necessary for the movement of ions and due to the closer position between them.

The ionic conductivities of polymer electrolytes containing 7.9 wt% of $LiClO_4$ are found in the order of $\sim 10^{-5}$ S/cm at room temperature. The SPEs with these conductivity values are interesting to be applied to electrochromic devices.

The variation of log conductivity and glass transition temperature as a function of salt concentration has been shown in Figure 7. The conductivities increase by increasing $LiClO_4$ content from 4 to 7.9 wt% of lithium salt. The increase in the ionic conductivity by increasing salt concentration can be related to the increase in the number of mobile charge carriers. The highest conductivity of 7.9 wt% of $LiClO_4$ doped system is consistent with DSC results, which



(a)

(b)

FIGURE 5 Bode plot of experimental (a) and equivalent circuit fitting data (b).

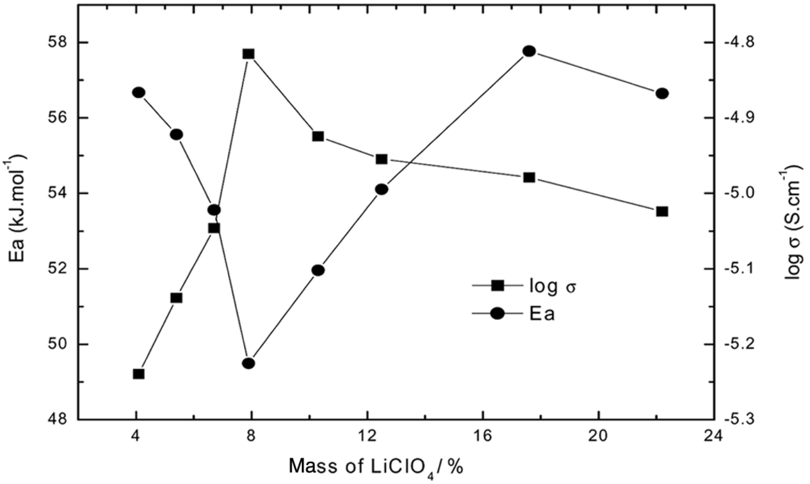


FIGURE 6 Variation of ionic conductivity and activation energy with $LiClO_4$ concentration.

show that 7.9 wt% of salt doped system have the lowest glass transition temperature with a lowest crystalline fraction. Fan *et al.* [15] reported that as the glass transition temperature decreases, the amorphous phase becomes more flexible and the ion conductivity should be enhanced. The conductivity at 22 wt% of salt concentration

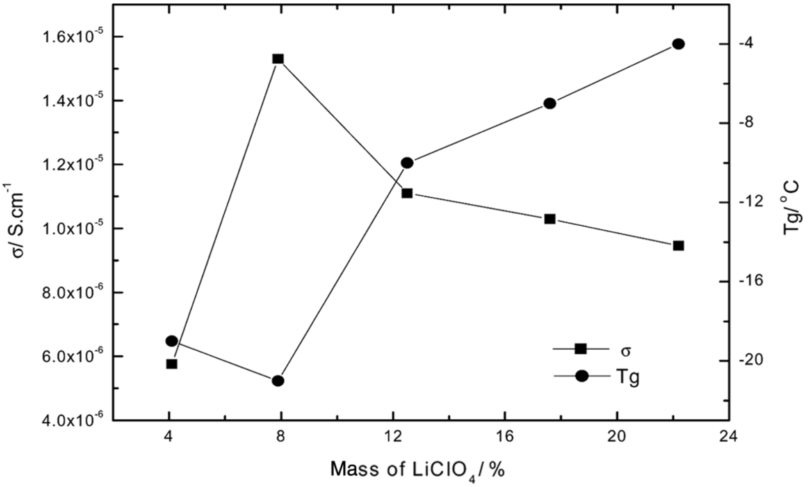


FIGURE 7 Effect of the lithium content on the conductivity and glass transition temperature of gelatin-based electrolyte.

indicates that the conductivity decreases at higher concentrations. The decrease in conductivity is consistent with increasing glass transition temperatures, as observed from the DSC analysis. The decrease in ionic conductivity at higher salt concentrations can be explained by the aggregation of ions, leading to the formation of ion clusters. Thus, a decrease in the number of mobile charge carriers increase the polymer electrolyte crystallinity.

CONCLUSIONS

Polymer electrolytes based on gelatin and $LiClO_4$ salt were prepared. The amount of lithium influences the electrolyte conductivity with a maximum for 7.9 wt% of $LiClO_4$. For this optimum concentration the values increase from 1.5×10^{-5} S/cm at room temperature to 4.9×10^{-4} S/cm at 80°C. The temperature dependence of the ionic conductivity exhibits an Arrhenius behavior with an activation energy of 49.5 kJ/mol.

The thermal analysis indicates that both glass transition temperature and crystallinity are low for the electroyte with 7.9 wt% of lithium salt.

REFERENCES

[1] Armand, M. (1994). *Solid State Ionics*, *69*, 309.

[2] Baskaram, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J., & Hattori, T. (2006). *Mater. Chem. Phys.*, *98*, 55.

[3] Wang, B., Feng, L., & Peng, X. (1991). *Solid State Ionics*, *48*, 204.

[4] Kim, D. W., Park, J. K., & Rhee, R. W. (1996). *Solid State Ionics*, *83*, 49.

[5] Prud'homme, J. & Robitaille, C. (1985). *Macromolecules*, *16*, 665.

[6] Stell, B. C. H. & Weston, J. E. (1982). *Solid State Ionics*, *7*, 75.

[7] Berthier, C., Gorecki, W., Minier, M., & Armand, M. B. (1983). *Solid State Ionics*, *11*, 91.

[8] Costa, R. G. F., Heusing, S., Avellaneda, C. O., Aegerter, M. A., & Pawlicka, A. (2006). *Mol. Cryst. Liq. Cryst.*, *447*, 363.

[9] Al-Kahlout, A., Pawlicka, A., & Aegerter, M. (2006). *Sol. Ener. Mater. Sol. Cells*, *90*, 3583.

[10] Dragunski, D. (2003). PhD Thesis, Universidade de São Paulo.

[11] Silva, M. M., Barros, S. C., Smith, M. J., & MacCallum, J. R. (2004). *Electrochim. Acta*, *49*, 1887.

[12] Ghiodelli, G., Ferloni, P., Magistris, A., & Sanesi, M. (1988). *M. Solid State Ionics*, *28–30*, 1009.

[13] Cowie, J. M. G. (1987). In: *Polymer Electrolytes, Reviews*, Mac Callum, J. R. & Vincent, C. A. (Eds.), Elsevier Applied Science: London, Vol. 1, 92.

[14] Kopitzke, R. W., Linkous, C. A., Anderson, H. R., & Nelson, G. L. (2000). *J. Electrochem. Soc.*, *147*, 1677.

[15] Lizhen, F., Ce-Wen, N., & Shujin, Z. (2003). *Solid State Ionics*, *164*, 81.