Multi-layered polymer electrolytes towards interfacial stability in lithium ion batteries

M. Aldissi[*]

Fractal Systems Inc., 14200 Carlson Circle, Tampa, FL 33626, USA

Abstract

Interfacial phenomena in lithium ion polymer batteries result in capacity fade upon cycling due to a number of reasons, with the major one being the poor electrode/electrolyte interface. This leads to poor chemical and electrochemical stability of the electrolyte, i.e. decomposition, electrode passivation, etc. In this paper, we describe a model system, which we have applied to a lithium ion battery for improving compatibility between electrodes and electrolytes in a truly solid-state system. This involved the fabrication of plasticizer-free multi-layered polymer electrolytes wherein the different layers have different compatibility characteristics with the electrodes. These characteristics include morphology, ionic and electronic mobility within the whole cell. Preliminary results using this approach are described. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Multi-layered polymer electrolyte; Interfacial stability; Lithium ion battery

1. Introduction

Lithium ion batteries have gained substantial interest in many application areas since the introduction of the liquid electrolyte-based Sony Energetic Inc.'s battery to the market [1,2] with an energy density exceeding 130 Wh/kg. Another more recent development consisted of the commercialization of Bellcore's laminated battery [3], which essentially uses liquid electrolytes and is being marketed by Ultralife. With the progress made in polymer electrolytes, the polymer lithium ion battery is expected to be the power source of choice for a variety of uses, including the next generation of lightweight consumer electronics, and electric and hybrid vehicles. Therefore, replacement of liquid electrolytes by a polymer equivalent with at least equal performance figures is a must for meeting the various end use requirements.

Interfacial phenomena in lithium ion polymer batteries result in capacity fade upon cycling due to a number of reasons, with the major one being the poor electrode/electrolyte interface. This leads to poor chemical and electrochemical stability of the electrolyte, i.e. decomposition, electrode passivation, etc. The various interfacial phenomena are usually magnified under non-ambient conditions

such as low or high temperatures. In order to achieve viability of the truly solid-state polymer lithium ion battery, several criteria need to be met and include good interfacial stability, high ionic conductivity with low activation energy, high lithium ion transport number and high thermal, chemical and electrochemical stability.

Several approaches have addressed these problems including the use of different polymer systems [4–8] and composites [9–11], as well as the use of plasticizers [12–17]. Most polymers had low ionic conductivities or high crystallinity or decomposed upon cycling. The polymer gel electrolytes, which have the highest ionic conductivities, have limited electrochemical stability upon cycling and require a suitable packaging. Other attempts included surface modification of graphite with some degree of success towards improving the interface [18]. The generation of functional groups such as –C=O, –COOH and –OH resulted in a better compatibility with the electrolyte. Although some significant advances have been made, there is no clear evidence that any of the systems have met all the requirements necessary for a successful solid-state polymer lithium ion battery.

To address the interface-related issues, we have used what is termed the ''mixed conductivity'' approach, which consists in our case of combining at the molecular level ionically and electronically conductive polymers in one for modification of the interface between the electrolyte and the two

* Tel.:+1-813-854-4332; fax: +1-813-854-5596.
E-mail address: fractals@infobridge.com (M. Aldissi).

electrodes. The hypothesis that an ionically conducting polymer is more likely to interface efficiently with an electronic conductor that has similar ionic species is not foreign. For example, compatibility of a substituted poly-pyrrole with one or several oxyethylene units is better than with the unsubstituted one due to the interaction between oxyethylene units on the polymer cathode and those of poly(ethylene oxide)-based electrolyte in conjunction with a lithium metal anode [19,20]. We have taken advantage of this aspect for the modification of well-established electrode materials such as carbon anodes and inorganic oxide cath-odes such as $LiCoO_2$.

2. The model system

Since total electrical separation between the two electro-des is necessary to minimize or avoid self-discharge, an additional layer consisting of a polymer based on the same ionic component that is incorporated in the mixed conduc-tivity material has been used in the middle of the cell. One can envision the resulting polymer electrolyte as a three-layer membrane at the macroscopic level, yet the actual picture can be translated by a progressive departure from a mixed conductor at the electrode interface towards a fully ionic conductor away from the electrode surface. It is worth noting though, that the electrodes *do not* consist of mixed powders as is typically done with blends. This is rather an interpenetrating network (IPN) that does not result in the modification of the electrode's electronic properties. A schematic of the electrodes/electrolyte assembly (not to scale) is shown for illustration in Fig. 1. Continuity of electrical and ionic conduction is provided in this approach. One can envision this continuity in the form of a decrease in electrical conductivity when departing from the electrode interface, and this is accompanied by a concomitant increase
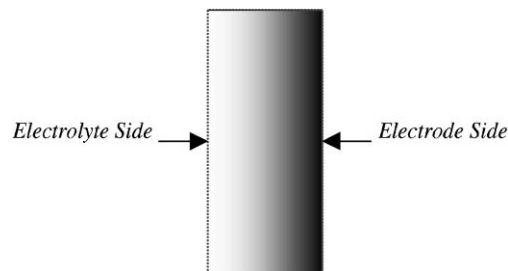

Fig. 2. Schematic of the gradient conductivity approach.

in ionic conductivity. Gradient conductivity in sorts is a better description. The pattern of Fig. 2 gives a general idea for this description.

A brief discussion of the above components follows with the aim of clarifying what materials we have selected for the above components and why. Although electrolyte and inter-faces, among several other parameters, are responsible for what is known as capacity fade problems associated with polymer lithium ion batteries and make up the key issues of our investigation, we will mention the appropriate electrodes used in this work.

2.1. The mixed conductor

One of the advantages of inherently conducting polymers is the possibility of varying their E_g as well as ε_f, by grafting substituents on the monomer repeat unit with groups of varied length and nature. Another added advantage of this modification is the induced processability of the resulting materials, an important characteristic for this work. Thus, an ionomer segment of a given length is added to the conduct-ing polymer on each repeat unit. We have chosen to work with environmentally stable materials and consist of sub-stituted polythiophenes for reasons that will be enumerated
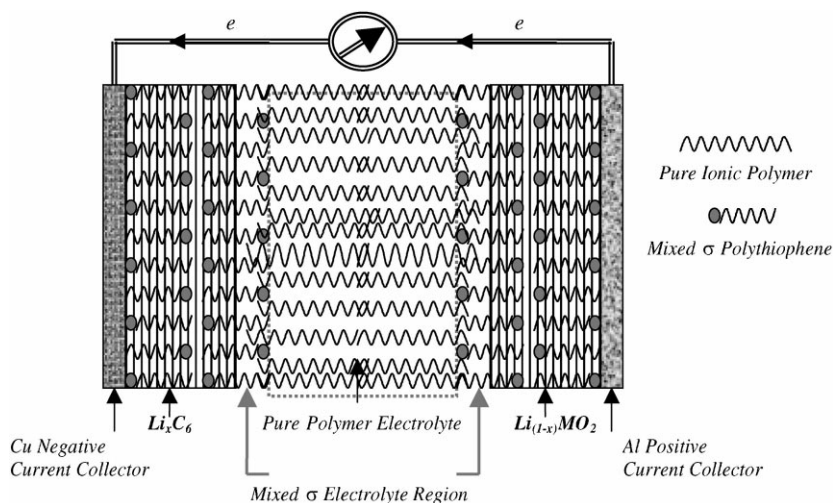

Fig. 1. Schematic of the mixed conductivity approach for electrode/electrolyte assembly.
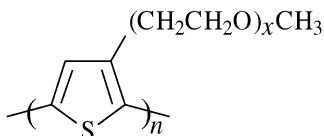
$(CH_2CH_2O)_xCH_3$

Fig. 3. Structure of an ionomer-substituted polythiophene.

shortly. A schematic of a mixed conductivity polythiophene structure is shown in Fig. 3.

The choice of this class of material derives from the ease of synthesis, variation of the chemical potential, and variation of ionic and electrical conductivity. It is known that a segment of four ethylene oxide units or higher is necessary to propel Li^+ in motion in an amorphous matrix [21]. The solvation continuum provided by these units, almost irrespective of the polymer structure, provides the best compromise in terms of ionic conductivity and solvation. However, our intent of using such materials is for interfacial compatibility and stability purposes. Therefore, even polythiophenes substituted with greater than four ethylene oxide or methylene oxide units can qualify for this purpose. Few examples for the ionomer substituent are given below (Table 1) with the oxidation potentials versus lithium, electrical conductivity and maximum optical absorption, respectively, of the corresponding polythiophene [22].

Firstly, it is obvious that the polyether component with the higher number of oxygen atoms will have a better ionic conductivity. As interfacial components, their high electrical conductivity promotes electron transfer within the electrode material. Meanwhile, a high ionic conductivity promotes ionic transfer. At the same time, as we depart from the electrode interface, a high electrical conductivity is not as important any more. Therefore, a polythiophene with an ionomer having greater than four oxygen atoms ($-(CH_2CH_2O)_xCH_3$, with $x = 4-8$) is an ideal material for this purpose, and is synthesized using a similar technique to that used for the above tabulated compounds [23]. As long as the first oxygen atom is two carbon atoms away from the thiophene ring, electrical conductivity, redox potential or band gap does not vary greatly. However, lithium transport is typically more efficient as x increases.

Secondly, another important point, particularly for the IPN component, is the good match between the chemical potentials of the mixed conductor and the electrode material so that the voltage profile upon charge or discharge is not altered. With an oxidation potential > 4 V versus Li, ε_f of

the mixed conductivity polythiophene is similar to that of the manganese spinel and of $LiCoO_2$. Thirdly, this class of polythiophenes can be reduced as well, with stable reduction potentials close to that of the carbon anode. Thus, the polymer in the IPN layer can undergo intercalation–deintercalation with similar energetics to those of the anode and cathode materials that we have used in our experiments, while maintaining the lithium ion transport properties because of its ionomer component. In other words, the energy band diagram remains practically unchanged.

Fourthly, with respect to its role at the interface with the purely ionic conductor, the mixed conductivity is necessary for a smooth transition from an electrical conductor (electrode) to an electrical insulator (polymer electrolyte). Compatibility between the mixed conductor and the ionic conducting layer is a must for making this transition energetically possible.

3. Experimental

3.1. Mixed conductivity polymer

The substituent consists of eight ethylene oxide repeat units ($x = 8$) so that segmental motion of this short alkoxy chain is significant enough to aid in ionic transport. The separation between the first oxygen atom and the ring is made of two CH_2 units as this proved to yield better electrical conductivity than when the spacer group is one CH_2 unit [22]. The monomer and polymer were synthesized by Leclerc at Laval University (Québec) [24]. The reaction scheme for monomer and polymer synthesis is shown in Fig. 4.

3.2. Ionically conducting polymer

The purely ionic polymer electrolyte consists of a blend made of a PEO having a M_w of 8000 (semi-crystalline or polycrystalline) and three low molecular weight PEGs (amorphous, with varied viscosity). The amorphous components consist of PEGDME having a molecular weight M_n of 250, 500 and 750 with a volume ratio of 1:1:1. The three PEGs are first dissolved in de-ionized water in an ultrasonic bath. In a separate vessel, PEO is dissolved in a similar manner. The contents of the two vessels are then mixed together in an ultrasonic bath for several hours to ensure a good homogeneity of the blend. The PEO:PEGs volume ratio is 1:4. To this solution, 3 wt.% of the total polymer composition of an interfacial modifier (γ-$LiAlO_2$) and 3 wt.% of a gelling agent are added and mixed in the ultrasonic bath. Finally, the lithium salt $LiN(CF_3SO_2)_2$ with an O:Li ratio of 8:1 is added and sonicated further for several hours. Sonication is used in our process in order to achieve not only complete dissolution, but also to enhance disorder of the crystalline phase. This polymer solution is then processed into thin membranes for characterization as such

Table 1
Selected properties of mixed conductivity poly(alkoxythiophenes)

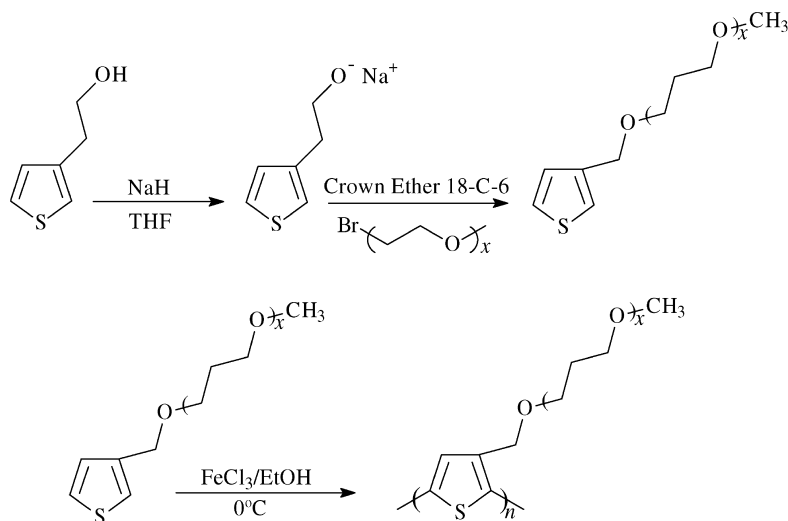| Ionomer substituent	E_{ox} (vs. Li)	σ (S/cm)	λ_{max} (nm)
$-CH_2OCH_2CH_3$	4.16	10	460
$-(CH_2)_2O(CH_2)_2OCH_3$	4.38	10^{-3}	420
$-CH_2O(CH_2)_2O(CH_2)_2OCH_3$	4.08	250	550
$-(CH_2)_2O(CH_2)_2O(CH_2)_2OCH_3$	4.08	10	440

Fig. 4. Synthesis reaction scheme of the ionomer-substituted thiophene monomer and polymer.

and in conjunction with the modified electrodes. A room temperature ionic conductivity of 10^{-3}–10^{-4} S/cm has been obtained. The high conductivity indicates that the crystalline order in PEO is significantly disrupted by the amorphous component. Composition of the latter is intended for promoting ionic motion while viscosity is kept high. The above mixture yields a material with solid-state mechanical characteristics.

3.3. Battery assembly

Both carbon anode and $LiCoO_2$ cathode materials were purchased from E-Tek (Natick, MA), with the current collectors and contacts attached. The two electrodes are immersed overnight in a 5 wt.% solution of the mixed conductivity polythiophene in tetrahydrofuran (THF). The electrodes are then removed from this solution and dried under vacuum. One should keep in mind that a thin layer of the mixed conductor is formed on the surface of the electrodes intentionally to provide for the continuity and gradient conductivity we discussed earlier. The two modified

electrodes and the pure ionic conductor membrane are laminated together.

3.4. Characterization

Ionic or electronic conductivity of the polymer electrolyte and mixed conductor was determined from the Nyquist plot and electrochemical characteristics of the cell were measured using a potentiostat/galvanostat (CH Instruments).

4. Result and discussion

Fig. 5 shows the Nyquist plots for the polythiophene ionomer and the pure ionic polymer described in Section 3. Volume conductivity determined from these plots is approximately 10 and 7×10^{-4} S/cm for the polythiophene derivative and the polymer electrolyte, respectively. Because of the ionomer segment in polythiophene, the measured value is a composite of both electronic and ionic conductivities. As can be seen from these plots, the diffusion
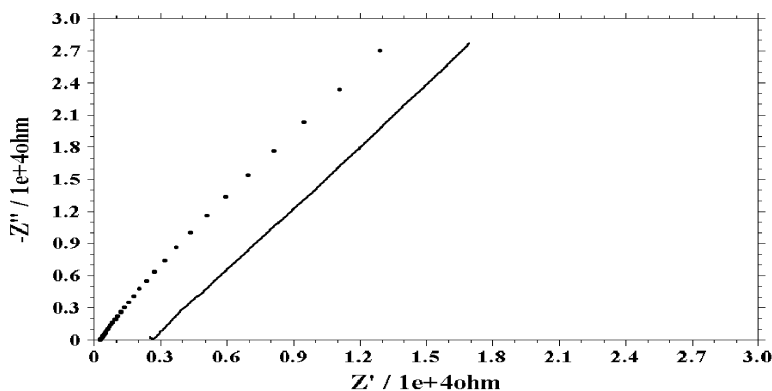

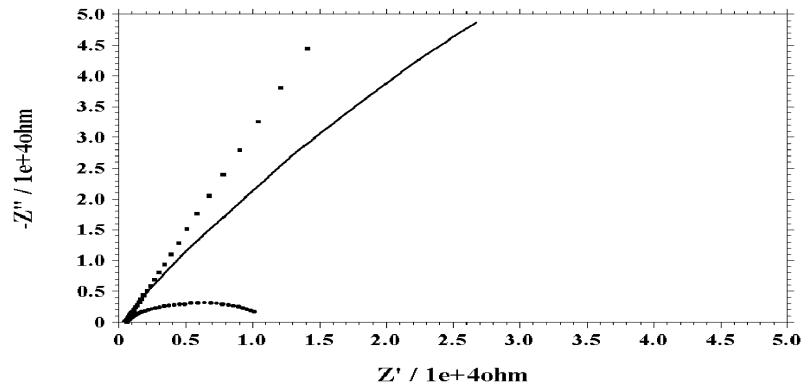Fig. 5. Nyquist plots of the multi-layer polythiophene ionomer (●) and pure ionomer (—).

Fig. 6. Nyquist plots of the multi-layer electrolyte at the rate of 0 V (■), 2.5 V (—) and pure ionomer at the rate of 2.5 V (●).

component is quite strong in both materials, which lead us to believe that the ionic segment of polythiophene plays a major role in lithium ion transport. In order to check stability of the polymer electrolyte, the membranes were submitted to a bias of 2.5 V versus lithium. The results show the Nyquist plots for the multi-layer electrolyte (according to Fig. 1) at no bias, and at 2.5 V (Fig. 6). The plot for the pure ionomer, in a similar configuration is also shown for comparison. It is clear that stability of the multi-layered electrolyte is stable at this voltage with very little curvature in the plot at low frequencies. The semi-circle observed for the pure ionomer at the same voltage is indicative of its poor electrochemical stability.

To gauge the effectiveness of our model on the battery performance, we have characterized a cell assembled as explained in Section 3 using the above components. Fig. 7 shows a typical charge/discharge plot of the battery (voltage versus capacity). The plot's profile is similar to what is observed in lithium ion batteries in general. However, the capacity values are higher than in conventional systems. Another important feature we wanted to test is cycling of the battery and whether capacity fade, normally observed in
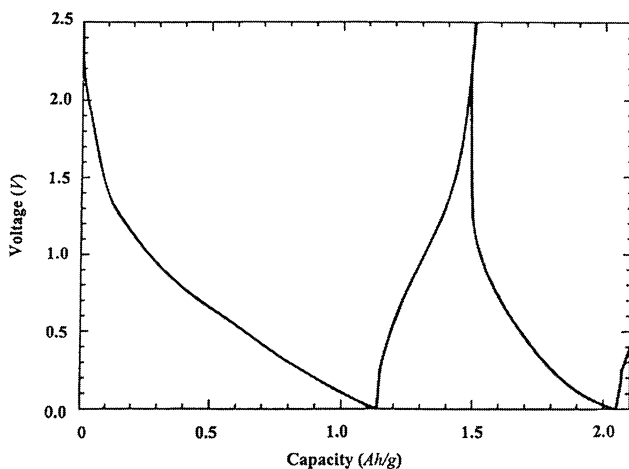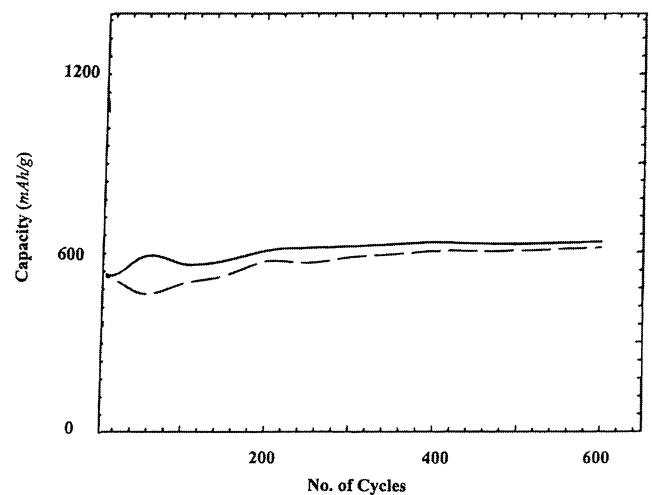

Fig. 8. Cycling performance of multi-layered polymer electrolyte based lithium ion battery.

lithium ion batteries, is observed in our system. The high capacity numbers shown in Fig. 8 are indicative of stability of the battery as well as the efficient lithium ion transfer throughout the electrodes' surface area. The capacity is almost constant for a large number of cycles, and this indicates that the IPN has contributed to stabilization of the interface that is typically partially responsible for capacity fade.

5. Conclusions

The overall characteristics of the lithium ion battery in the conventional sense depend on the relative energies of its components. With the use of a mixed conductor as described in our approach, the same conventional picture applies except that the Fermi level of the anode ($\varepsilon_f(A)$) and cathode materials ($\varepsilon_f(C)$) are replaced by the Fermi levels of their corresponding junctions formed with the mixed conductor as shown in Fig. 9, where $\varepsilon_f(A)$ is the Fermi level of the polythiophene ionomer/carbon junction and $\varepsilon_f(C)$ is the Fermi level of the polythiophene ionomer/LiCoO$_2$ junction.

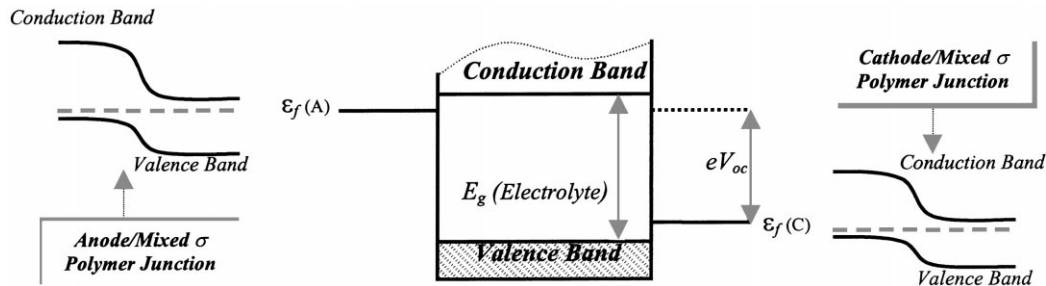Fig. 7. Charge/discharge of lithiated carbon/multi-layered polymer electrolyte/LiCoO$_2$ battery.

Fig. 9. Relative energies of the electrolyte window E_g and the IPN electrode potentials.

Based on the preliminary results obtained here, we can conclude that a mixed conductivity polymer interfacing with the main electrode materials can facilitate ion mobility as well as electron transfer, thus making the charge/discharge processes take place with high efficiency. One key element is the high electronic conductivity of the mixed conductivity polymer so that electron transfer is not subjected to high potential barriers at the microscopic level within the IPN electrode.

Acknowledgements

References

[1] Y. Nishi, H. Azuma, A. Omaru, US Patent 4959281, September 25, 1990.

[2] B.A. Johnson, R.E. White, J. Power Sources 70 (1) (1998) 48.

[3] J.M. Tarascon, G.G. Amatucci, C. Schmutz, A.S Gordz, P.C. Warren, F.K. Shokoohi, in: Proceedings of the eighth International Meeting on Lithium Battery, Nagoya, Japan, June 1996, Abstract I-C-1.

[4] C.A. Vincent, Chemistry in Britain, April, 1981, p. 391.

[5] M. Armand, Adv. Mater. 2 (1990) 278.

[6] J. MacCullum, C.A. Vincent (Eds.), Polymer Electrolyte Review I & II, Elsevier, Amsterdam, 1987.

[7] F. Gray, Solid Polymer Electrolytes, VCH, 1991.

[8] M. Armand, J.Y. Sanchez, M. Gauthier, Y. Coquette, in: J. Lopkowski, P.N. Ross (Eds.), Electrochemistry of Novel Materials, VCH, 1994, p. 65.

[9] E. Ruiz-Hitzky, Adv. Mater. 5 (1993) 334.

[10] E. Ruiz-Hitzky, P. Aranda, C. Galvan, Adv. Mater. 7 (1995) 180.

[11] P. Judeinstein, et al., Chem. Mater. 6 (1994) 127.

[12] K.M. Abraham, M. Almagir, J. Power Sources 44 (1993) 195.

[13] G. Nagasubramanian, A.I. Attia, G. Halpert, J. Appl. Electrochem. 24 (1994) 298.

[14] C. Schmutz, J.M. Tarascon, A.S. Gordz, P.C. Warren, F.K. Shokoohi, in: Proceedings of the Electrochemical Society Meeting, Miami, FL, October 1994, Abstract No. 109.

[15] G.B. Appetecchi, F. Croce, B. Scrosati, Electrochim. Acta 40 (1995) 991.

[16] G. Dautzenberg, F. Croce, S. Paaerini, B. Scrosati, Chem. Mater. 6 (1994) 538.

[17] G.B. Appetecchi, F. Croce, B. Scrosati, J. Power Sources 66 (1997) 77.

[18] E. Peled, et al., J. Electrochem. Soc. 143 (1996) L5.

[19] M.G. Minett, J.R. Owen, in: M. Aldissi (Ed.), Proceedings of the ICSM'88, Synth. Met. 28 (1989) C-211.

[20] C. Arbizzani, A. Marinagelli, M. Mastragostino, L. Meneghello, T. Hamaide, A. Guyot, J. Power Sources 43/44 (1993) 453.

[21] D. Baril, C. Michot, M. Armand, Solid State Ionics 94 (1997) 35.

[22] J. Roncali, Chem. Rev. 92 (1992) 711.

[23] M. Lemaire, R. Garreau, J. Roncali, D. Delabouglise, H. Korri, F. Garnier, New J. Chem. 13 (1989) 863.

[24] I. Lévesque, M. Leclerc, Chem. Mater. 8 (12) (1996) 2843.