An electrochemical investigation on polyvinylidene fluoride-based gel polymer electrolytes

P. Periasamy[a],*, K. Tatsumi[b], M. Shikano[b], T. Fujieda[b], T. Sakai[b], Y. Saito[b], M. Mizuhata[c], A. Kajinami[c], S. Deki[c]

[a]*Central Electrochemical Research Institute, Karaikudi 630 006, India*
[b]*Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan*
[c]*Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657, Japan*

Abstract

Many types of polymer electrolytes have been developed and characterized in the past few years. Recently special attention has been focussed on the development of gel polymer electrolytes consisting of host polymers such as PAN, PVC, PVP, PVS, PMMA, PEGDA and PVdF etc., as they may find unique applications in consumer electronic and electric vehicle products. In the present study, gel polymer electrolytes have been prepared using the solvent casting technique in the presence of PVdF-1015 (SOLEF), EC + PC as a plasticizer, and LiBF$_4$ salt. The influence of the amount of polymer, plasticizer and LiBF$_4$ on the gel electrolytes has been studied using XRD, DSC, AC impedance and charge–discharge studies. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Lithium metal free lithium batteries have been known for several years and were originally termed 'rocking chair batteries' by Armand. In 1990, Sony Energy Tech [1] announced the commercial availability of the lithium-ion rechargeable battery with a carbon–non-graphite anode and a LiCoO$_2$ cathode. The characterization of ionically conducting polymeric membranes have provided the interesting possibility of developing new types of lithium batteries having a thin-layer laminated structure. Various academic and industrial laboratories [2–5] are presently engaged in the development of ion conducting polymer batteries. Today, the lithium polymer battery is a valid candidate for the consumer electronics market, and for electric vehicles as a replacement for nickel–cadmium and lead-acid batteries. In the present work, results of a detailed investigation on gel polymer electrolytes prepared from PVdF, EC + PC and LiBF$_4$ salt are reported.

2. Experimental

2.1. Optimization of gel polymer electrolyte composition

Gel polymer electrolyte films were prepared and examined for their homogeneity, dimensional stability and ease of preparation.

*Corresponding author. Fax: +91-4565-37779.

2.2. Preparation of gel polymer electrolyte films

Gel polymer electrolyte films were prepared by heating a mixture of PVdF-1015 (SOLEF), EC + PC and LiBF$_4$ salt in a pyrex bottle at 160–175°C for 60–75 min. The resulting homogeneous, viscous solution was poured on a PET sheet and the desired thickness was made using a scalpel. The casting film was dried in a dry room for 3–4 h. A dimensionally stable and solvent-free polymer electrolyte film with a thickness of 75 μm was obtained.

2.3. Preparation of the composite cathodes

Composite cathodes were prepared by the addition of 50% LiCoO$_2$ and 15% graphite (KS-15) to a mixture of suitable composition of 35% gel polymer electrolyte which consists of PVdF, EC + PC and Li salt. Powders were added to the gel while hot and mechanically blended. The blended paste was poured onto the aluminium foil and spread uniformly using a scalpel. Composite cathodes were dried at 130°C for 24 h. The area of the electrode was 2 cm^2.

2.4. Thermal measurement analysis

The thermal stability of the gel polymer electrolyte, and the raw materials such as PVdF and LiBF$_4$ were investigated using Differential Scanning Calorimeter (DSC-SEIKO, TA Station SSC-5000 series) in an argon gas flow. The heating rate was10°C min^{-1} and the samples were scanned in the range 30–300°C.

2.5. X-ray diffraction measurements

The X-ray diffraction patterns of PVdF, LiBF$_4$ and gel polymer electrolyte films were obtained by means of X-ray Diffractometer (Rigaku) with CuKα radiation.

2.6. Electrochemical studies

2.6.1. Impedance measurements
The AC impedance measurements were carried out on a gel polymer electrolyte thin film sandwiched between two blocking electrodes. We used SS–gel polymer electrolyte–SS with a Solartron SI 1286

electrochemical interface coupled with an SI 1260 impedance gain phase analyzer over the frequency range 1 Hz–100 kHz at room temperature and 0.01 V AC signal. All the experiments were repeated in order to confirm that the results were reproducible.

2.6.2. Transference number determination
The transference number was determined using the combination of the complex impedance and potentiostatic polarization measurements. The gel polymer electrolyte films were sandwiched between two metallic lithium electrodes.

2.6.3. Electrochemical interface stability
The stability of the Li interface in the gel polymer electrolyte film was studied by monitoring the AC impedance of a symmetrical cell, as a function of storage under open circuit conditions at room temperature.

2.6.4. Charge–discharge studies
The charge–discharge behavior of the composite cathode LiCoO$_2$ and Li metal anode with gel polymer electrolyte was studied at various current densities at various cycles.

3. Results and discussion

The gel polymer electrolyte films were determined using triangular composition diagrams as shown in Fig. 1. The gel electrolyte is represented as comprising of three components, namely polymer, plasticizer and Li salt. The intercepts on the three axes of the three arrows directed from the point representing the electrolyte composition give the wt.% of PVdF, EC + PC and LiBF$_4$ salt. All the compositions shown in Fig. 1 give the homogeneous solutions at 160–175°C. However, the solution containing more than 25% PVdF is too viscous and that containing less than 22.5% is too weak and fragile. Therefore, it cannot be used in practical battery applications.

The gel polymer composition, i.e. 22.5–25% PVdF-1015–60–65% EC + PC and 12.5–15% LiBF$_4$ exhibit good gel solvent-free film. The heating temperature and time of the precursor mixture can easily be controlled to prepare polymer films of reproducible compositions.
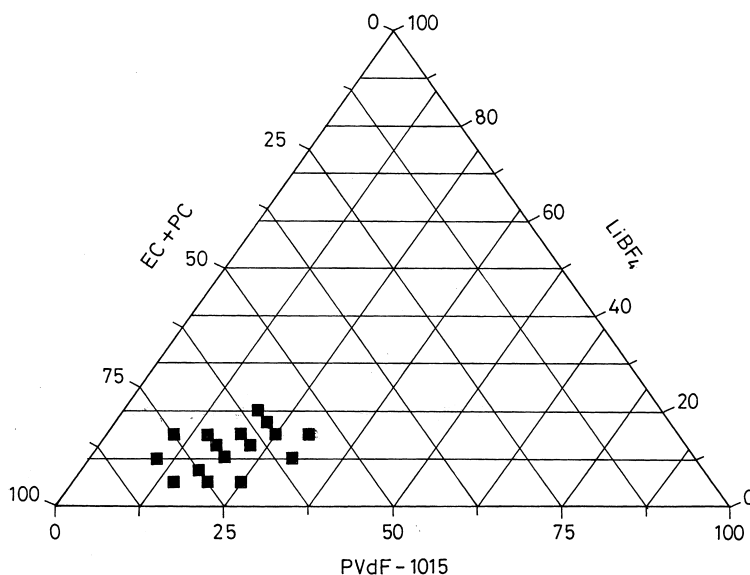
Fig. 1. Composition diagram for gel polymer electrolytes containing PVdF-1015 (SOLEF), EC+PC and the various LiBF$_4$ ratios by weight.

DSC plots for PVdF, LiBF$_4$, 22.5% PVdF–65% EC + PC–12.5% LiBF$_4$ and 25% PVdF–60% EC + PC–15% LiBF$_4$ are shown in Fig. 2. In Fig. 2(a) an endothermic peak in the range 145–180°C was shown, which can be the melting point of polymer. In the case of Fig. 2(b), the sharp endothermic peak at 105°C corresponds to the adsorption of water molecules. By increasing the LiBF$_4$ salt concentration as shown in Figs. 2(c) and (d), the phase transition of plasticizers were enhanced. The enhancement may be due to the strong interaction between the polymer chain and lithium salts.

Fig. 3 shows the X-ray diffraction pattern of PVdF, LiBF$_4$ and gel polymer electrolyte, respectively. The X-ray diffraction patterns reveals clearly that the addition of the plasticizers EC + PC reduce crystallinity considerably in these experiments [Figs. 3(c) and (d)]. The plasticizers may induce significant disorder into the original polymer structure [6] and it is attributed to the interaction between the polymer and the solvents which results in gel polymer electrolytes with much lower crystallinity, as manifested by the broad diffraction peak centered at $2\theta = 20°$.

The gel polymer electrolyte resistance was determined from Cole-Cole plots of the resulting impedance data. Fig. 4 shows that the plot of the
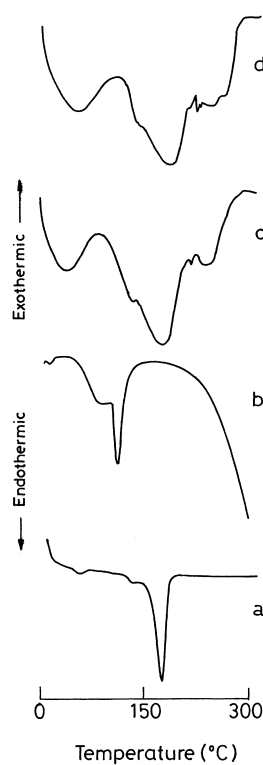

Fig. 2. DSC curves of: (a) PVdF-1015; (b) LiBF$_4$; (c) 22.5% PVdF-1015–65% EC+PC–12.5% LiBF$_4$; and (d) 25% PVdF-1015–60% EC+PC–15% LiBF$_4$.
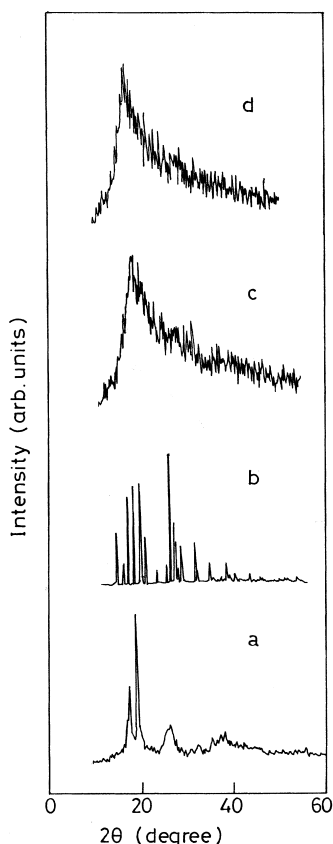
Fig. 3. X-ray diffraction patterns of: (a) PVdF-1015; (b) LiBF$_4$; (c) 22.5% PVdF-1015–65% EC+PC–12.5% LiBF$_4$; and (d) 25% PVdF-1015–60% EC+PC–15% LiBF$_4$.

imaginary part of the impedance vs. the real part consists of a slanted spike displaced from the origin. Here the resistance was measured from the high-frequency intercept on the real axis. The conductivity of the polymer electrolyte was calculated from the measured resistance and the known area and thickness of the polymer film. Similar conditions were maintained for all other experiments, as shown in Table 1. It can be seen from Table 1 that the conductivity of the electrolyte is mainly determined by the weight ratio of PVdF–EC + PC and the Li salt [7]. Raising the ratio automatically lowers the conductivity. The conductivity of 20% PVdF containing 70–75% EC + PC is 1.6–2.2×10^{-3} S cm^{-1}, but as the concentration of PVdF increases the conductivity becomes less. For a concentration of 27.5–30% PVdF with 60–67.5% EC + PC, the conductivity is

2.1×10^{-4}–1×10^{-3} S cm^{-1}. However, the addition of higher concentrations of plasticizers will enhance the conductivity. From these data, all the gel polymer compositions are predicted to have a conductivity within the range 10^{-4}–10^{-3} S cm^{-1}.

Fig. 5 shows the conductivity and mechanical stability of gel polymer electrolytes containing PVdF-1015 at room temperature. It can be proved that as the polymer content increases, the mechanical stability increases and the conductivity of the gel polymer decreases. As the polymer content decreases the conductivity increases and the corresponding gel polymer lowers the mechanical strength and the dimensional stability. Under a constant potential, the transient current $I(t)$ of a cell, Li–27.5% PVdF − 62.5% EC + PC − 10% LiBF$_4$–Li is expressed by

$$I(t) = V/(R_b + R_i) \qquad (1)$$

Where V is a constant applied potential. R_b and R_i are the bulk resistance and interfacial resistance, respectively [8]. Their values can be obtained from the complex impedance measurements. At, $t = 0$, cation and anion migration takes place, but when t tends to infinity, the current reaches an equilibrium state which is denoted by $I(\infty)$. At this time, the cations are the only mobile carriers. Then t_{Li+} can be easily derived from

$$t_{Li+} = R_b / [V/I(\infty) - R_i] \qquad (2)$$

Fig. 6(a) displays the current as a function of time for the cell under 10, 20, 30 and 50 mV. Fig. 6(b) is the impedance spectrum for the low- and high-frequency semicircle. Then the transference number t_{Li+} of the gel polymer can be calculated from Eq. (2), and t_{Li+} is found to be equal to 0.3. A comparison of the conductivity of different Li salts used in two types of weight ratio of gel polymer, such as 25% PVdF–60% EC + PC–15% LiBF$_4$ and 22.5% PVdF–65% EC + PC–12.5% LiBF$_4$, at different temperatures is shown in Table 2. It indicates that when the weight ratio of Li salts concentration increases the conductivity of the gel polymer electrolyte decreases slightly. Secondly, as the temperature increases the corresponding gel polymer conductivity is also increased. Thirdly, an increase in the salt concentration in the gel polymer will increase the concentration of the charge carrier ions, which
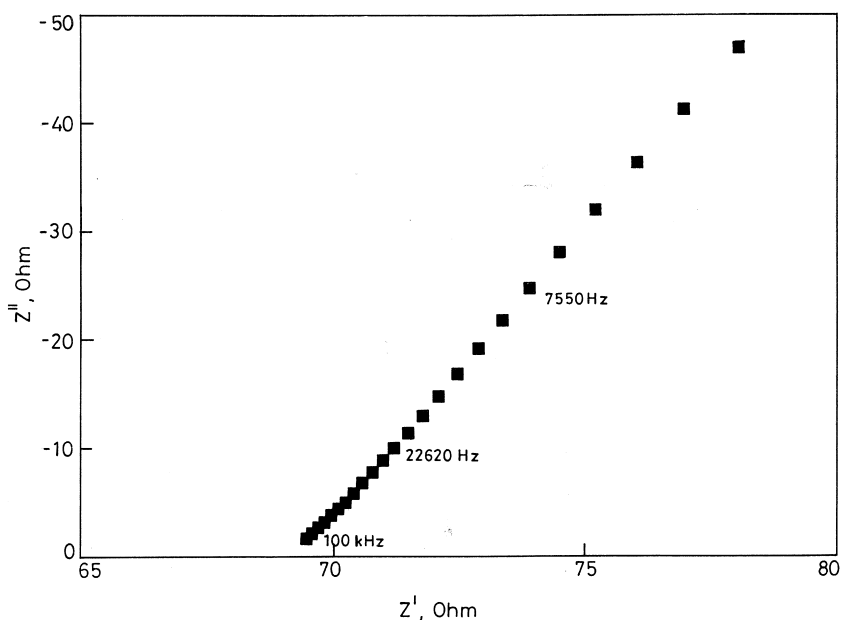
Fig. 4. Typical impedance plot of the 20% PVdF-1015–75% EC+PC–5% LiBF$_4$ gel polymer electrolyte at room temperature.

Table 1
Composition in wt.% w/o and conductivity of PVdF-1015 (SOLEF), EC+PC and LiBF$_4$ gel polymer electrolytes

Sample no.	PVdF-1015	EC	PC	LiBF$_4$	Conductivity (S cm^{-1})
A	10	40	40	10	0.00132
B	10	37.5	37.5	15	0.00113
C	15	40	40	05	0.00124
D	15	35	35	15	0.00073
E	17.5	37.5	37.5	7.5	0.00116
F	17.5	35	35	12.5	0.00072
G	20	37.5	37.5	05	0.00100
H	20	35	35	10	0.00071
I	20	32.5	32.5	15	0.00048
J	20	30	30	20	0.00069
K	22.5	32.5	32.5	12.5	0.00075
L	25	35	35	05	0.00097
M	25	30	30	15	0.00034
N	30	32.5	32.5	10	0.00018
O	30	30	30	10	0.00010

should have a positive effect on the conductivity. It will also increase the viscosity, which will lower the mobility of the charge carriers. Therefore, the conductivity of the gel polymer electrolyte is the result of interplay between the concentration of its charge carrier and their mobility, determined by the polymer–plasticizer ratio and the salt concentration.

The passivation phenomena at the lithium inter-face in the gel polymer electrolytes has been studied by monitoring the impedance response of a symmetrical cell, kept under open circuit for a period of 9 days at room temperature. The stability of the gel polymer electrolyte and the morphological model of the lithium passivation layer are shown in Figs. 7(a) and (b), which compares on an expanded scale the time of evolution of the bulk electrolyte, R_b, and
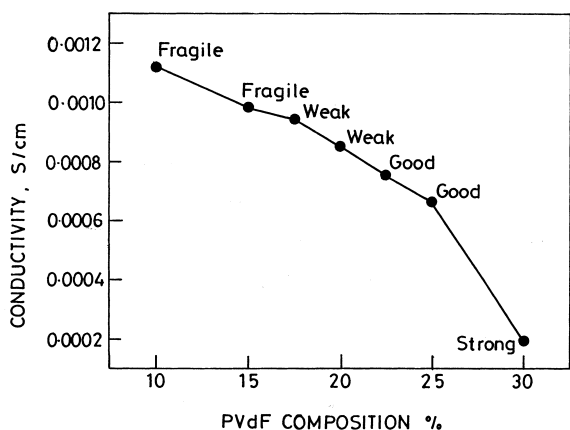
Fig. 5. Conductivity and mechanical stability of gel polymer electrolytes containing EC+PC, LiBF$_4$ and PVdF-1015 at room temperature.

the resistance of the passivation film, R_f. In accordance with the model proposed by Alamgir and Abraham [9], the large semicircle is attributed to the parallel combination of the resistance (R_f) and the capacitance associated with the passivation film on the lithium electrode, and the small semicircle is attributed to the charge transfer resistance imposed parallel to the double layer capacitance.

The intercept of the large semicircle at the high-frequency side on the Z' axis gives the resistance of the bulk electrolyte. It can be obtained from Figs. 7(a) and (b) that R_b values remain constant below 4 Ω during the entire period of storage. This is due to the stability of the gel polymer which did not change its original composition either through plasticizer solvent evaporation or some reaction with the Li electrode [10]. The R_f determined from the intercept of the large semicircle at the lower frequency side on the real axis, gradually increased between Figs. 7(a) and (b). The increase in R_f is presumably caused by the uniform growth of the passivation film formed from the reaction between the lithium and the gel polymer electrolytes.

The typical capacity–rate behavior of a cell Li–LiCoO$_2$ with 25% PVdF–60% EC+PC–15% LiBF$_4$ gel polymer electrolyte at room temperature is shown in Fig. 8. At 25 μA cm^{-2}, the cell delivers about 90–50% of the cathode capacity. The cell could be further discharged at various current densities such
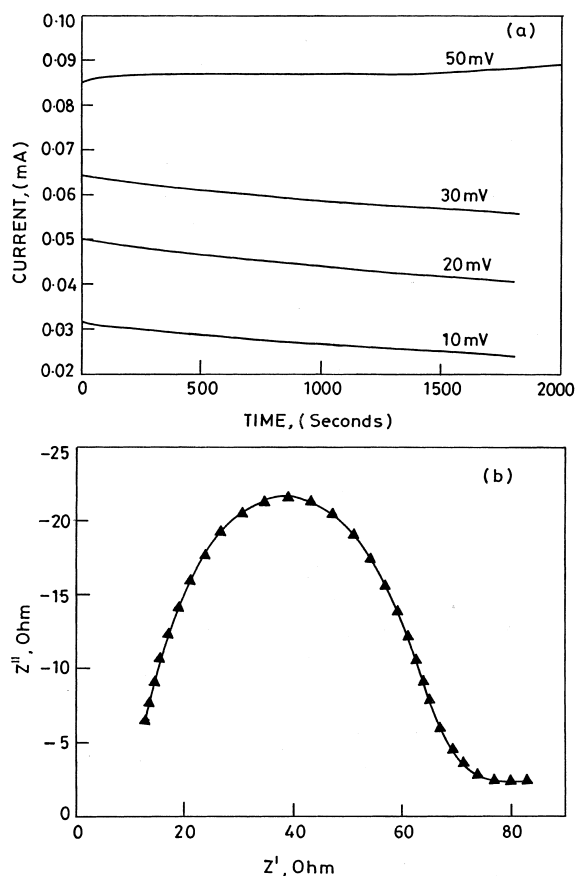

Fig. 6. (a) Polarisation current as a current function of time; and (b) AC impedance spectrum of Li–27.5% PVdF-1015–62.5% EC+PC–10% LiBF$_4$ gel polymer electrolyte–Li.

as 50, 75 and 100 μA cm^{-2}. At 100 μA cm^{-2}, 17–7% of the cathode capacity was attained from 210–310 cycles.

4. Conclusions

1. A homogeneous viscous stable solvent-free gel polymer electrolyte film of composition 22.5–25% PVdF–60–65% EC+PC–12.5–15% LiBF$_4$ was obtained.
2. The phase transitions of EC and PC were observed and were enhanced by increasing the concentration of the Li salt and the polymer.
3. By the addition of plasticizers to the polymer, the

Table 2
Temperature performance vs. conductivity of gel polymer electrolyte compositions

Sample no.	Gel electrolyte compositions	Temperatures ($S\ cm^{-1}$)	Conductivity
1	25% PVdF–60% EC+PC–15% LiBF$_4$	20°C	0.00034
		40°C	0.00068
		65°C	0.00124
2	22.5% PVdF–65% EC+PC–12.5% LiBF$_4$	20°C	0.00075
		40°C	0.00100
		65°C	0.00313

Fig. 8. Capacity–rate behaviour of a Li–LiCoO$_2$ cell containing 25% PVdF-1015–60% EC+PC–15% LiBF$_4$ gel electrolyte at room temperature.

4. A conductivity of the order of 10^{-4}–10^{-3} S cm^{-1} was achieved for the gel polymer electrolyte.
5. The resistance of the lithium passivation film, R_f, continuously increases with increasing concentration of salt and polymer, thus suggesting the formation of a passivation layer with a homogeneous structure.
6. The capacity–rate behavior is decreased by the formation of a passivation layer with the lithium metal anode and the gel polymer electrolytes.
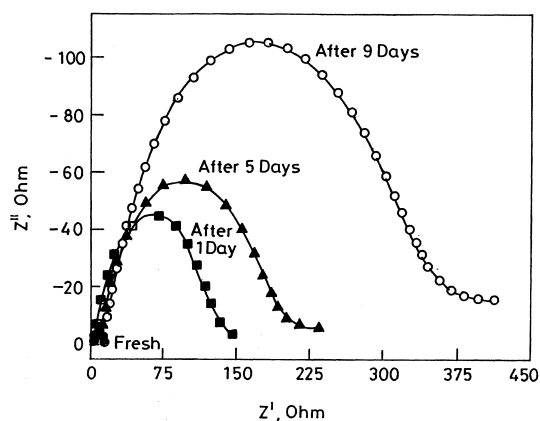
Fig. 7. (a) The impedance plots of a Li–25% PVdF-1015–60% EC+PC–15% LiBF$_4$–Li cell stored at room temperature; and (b) the impedance plots of a Li–22.5% PVdF-1015–65% EC+PC–12.5% LiBF$_4$–Li cell stored at room temperature.

original structure of the polymer was changed into a less crystalline structure as manifested by the broad diffraction peaks obtained.
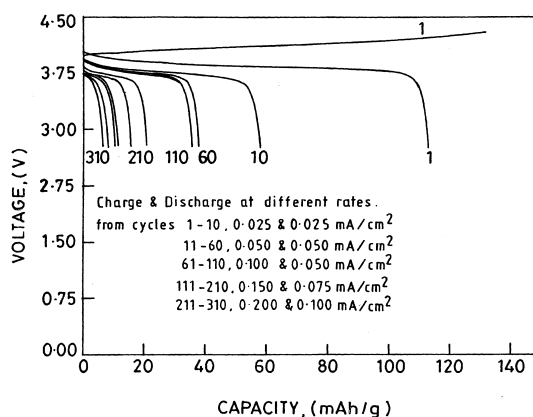
Acknowledgements

References

[1] Sony lithium-ion battery performance summary, JEC Battery, Newsletter 2 (1994) 31.

[2] A. Hooper, J.M. North, Solid State Ionics 9 (1983) 1161.

[3] B. Scrosati, in: J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Review, Vol. 1, Elsevier Applied Science, London, 1987, p. 315.

[4] J.S. Lundsgoard, S.Y. de-Anderson, R. Koksbang, in: B. Scrosati (Ed.), Proc. 2nd Intl. Symp. on Polymer Electrolytes, Elsevier, New York, 1990, p. 395.

[5] M. Gautheir, A. Belanger, B. Kapfer, in: J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Review, Vol. 2, Elsevier Applied Science, London, 1989, p. 285.

[6] M. Armand, W. Gorecki, R. Andreani, in: B. Scrosati (Ed.), Proc. 2nd Intl. Symp. on Polymer Electrolytes, Elsevier, New York, 1990, p. 91.

[7] Z. Jiang, B. Carrol, K.M. Abraham, Electrochim. Acta 42 (1997) 2667.

[8] P.C. Warren, O.S. Gebizlioglu, F. Shokooohi, Proc. 10th Annu. Battery Conf., USA, Jan. 1995.

[9] M. Alamgir, K.M. Abraham, J. Power Sources 54 (1995) 40.

[10] G.B. Appetechi, G. Dautzenberg, B. Scrosati, J. Electrochem. Soc 143 (1996) 6.