

Short communication

# Structural and electrochemical properties of micro-porous polymer blend electrolytes based on PVdF-co-HFP-PAN for Li-ion battery applications

A. Subramania\*, N.T.Kalyana Sundaram, G.Vijaya Kumar

*Department of Industrial Chemistry, Alagappa University, Karaikudi 630003, India*

Received 18 November 2004; accepted 12 December 2004

Available online 15 November 2005

## Abstract

A micro-porous polymer blend electrolyte based on polyvinylidene fluoride-co-hexa fluoropropylene (PVdF-co-HFP) and polyacrylonitrile (PAN) was prepared by phase inversion technique with different compositions. The ionic conductivity of micro-porous polymer blend electrolyte films were studied by varying the PAN content in the (PVdF-co-HFP) matrix. It was observed that the ionic conductivity of micro-porous polymer blend electrolyte increases with increase in PAN content. The effect of lithium salt concentrations was studied for the micro-porous polymer blend electrolyte by measuring the conductivity at different temperatures in the range of 301–353 K. The micro-porous polymer blend electrolyte was subjected to XRD, SEM and TG/DTA analysis to determine the amorphosity nature, surface morphology and thermal stability of the polymer electrolyte, respectively. Linear sweep voltammetry and dc-polarization studies were also performed to find the stability and lithium transference number of micro-porous polymer blend electrolyte, respectively. Finally, charge–discharge studies were carried out in an assembled cell with carbon anode and  $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  cathode and micro-porous polymer blend electrolyte in between the above electrodes.

© 2005 Published by Elsevier B.V.

*Keywords:* Micro-porous polymer electrolyte; Ionic conductivity; PVdF-HFP; Linear sweep voltammetry; Charge–discharge studies

## 1. Introduction

In recent years, there has been a growing demand for high-energy density rechargeable lithium batteries for portable electronic products because of their advantages including safety, high-energy density, high single cell voltage, geometry and no memory effect. However, the ionic conductivity of polymer electrolytes is generally low, often too low for practical application. To improve the basic requirements of the polymer electrolyte, various processes have been used such as electrochemical stability towards lithium battery electrodes, compatibility with the electrode materials, reasonable ionic conductivity, sufficient thermal stability and good mechanical stability. General methods for preparing the gel polymer electrolytes require a moisture-free environment because of higher water sensitivity of lithium

polymer electrolytes prepared through this method cause the electrolytes to lose much of their mechanical strength. The mechanical properties of the film can be enhanced either by chemical or mechanical curing, which is expensive. In order to overcome these problems, a micro-porous polymer electrolyte is prepared for lithium batteries by a phase inversion process. A micro-porous polymer membrane is prepared and then soaked in an electrolyte solution and then investigated [1–4]. This membrane has a capability to absorb an electrolyte solution without leakage and has chemical compatibility with electrode materials and adhesive properties for adhering the electrodes to the micro-porous separator [5]. A few polymer candidates can meet the above requirements. Among the few polymers, polyvinylidene fluoride-co-hexa fluoropropylene (PVdF-co-HFP) was found to meet all the basic requirements of the polymer electrolyte [6,7]. But the ionic conductivity of PVdF-co-HFP based polymer electrolyte is not very good. In order to improve the ionic conductivity, an easily homogeneous hybrid film forming

\* Corresponding author. Tel.: +91 4565 225 205; fax: +91 4565 225 202.  
E-mail address: [a.subramania@rediffmail.com](mailto:a.subramania@rediffmail.com) (A. Subramania).

polymer like polyacrylonitrile (PAN) was chosen to blend with the above PVdF-co-HFP matrix in which the Li-salt, and plasticizer were molecularly dispersed [8]. A PVdF-co-HFP-PAN based polymer blend electrolyte has been developed.

In the present investigation, an attempt has been made to prepare micro-porous polymer blend electrolytes by a phase inversion process followed by adopting an activation process in which a polymer blend film is soaked in an electrolyte solution to get a polymer blend electrolyte. Finally, the structural and electrochemical properties of PVdF-co-HFP-PAN based micro-porous polymer blend electrolyte have also been investigated.

## 2. Experimental

PVdF-co-HFP with an average molecular weight of >500,000 (Aldrich, USA), PAN with an average molecular weight of >100,000 (Aldrich, USA) and LiClO<sub>4</sub> (E-Merck, Germany) were dried under vacuum oven at 100 °C under 10<sup>-3</sup> Torr pressure for 48 h. EC&DEC (Across Organic, Belgium) were purified by distillation under reduced pressure.

Different compositions of micro-porous polymer blend films were obtained by phase inversion techniques as described elsewhere [9,10]. The polymers PVdF-co-HFP and PAN were dissolved in DMF. The resultant viscous solution was spread as a film on a glass substrate using Doctors blade. Finally, the film was dried at 80 °C in a vacuum oven under 10<sup>-3</sup> Torr pressure for 3 h to remove any further traces of DMF. The thickness of the micro-porous film was in the range of 150–200 μm. The films were soaked in 1 M LiClO<sub>4</sub> in EC&DEC (1:1, v/v) for 18 h to get a micro-porous gel polymer electrolyte. Finally, the effect of salt concentrations was studied for the polymer electrolyte of the high ionic conductivity system.

The crystalline structure of the resultant micro-porous polymer blend electrolyte films was investigated by JOEL-X-ray diffractometer (JDX-8030). SEM studies were carried out with JOEL-Scanning electron microscope (JSM-35CF) to find the surface morphology of PVdF-co-HFP-PAN based polymer film, micro-porous polymer blend membrane and micro-porous polymer blend electrolyte. TG/DTA data were obtained between 0 and 700 °C employing Dupont-DTA/TG analyzer at the scan rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atm.

Conductivity measurements were performed by sandwiching the polymer electrolyte in between two stainless steel (SS) electrodes using EG&G electrochemical impedance analyzer over a frequency range of 10–100 kHz at various temperatures in the range of 25–80 °C. The electrochemical stability of micro-porous polymer blend electrolyte was evaluated with cell featuring stainless steel as working electrode and lithium as counter and reference electrode by linear sweep voltammetry at 25 °C. The cell was assembled in a dry box under argon atmosphere at a scan rate of 1 mV s<sup>-1</sup> was preferred to study the system under investigation.

The K.M. Abraham and Z. Jiang method is adopted to evaluate the transference number of micro-porous polymer electrolyte by placing the polymer electrolyte in between two symmetrical lithium metal electrodes as described previously [11,12].

Carbon and LiSr<sub>0.25</sub>Mn<sub>1.75</sub>O<sub>4</sub> were employed as negative and positive electrodes, respectively. The laminated cell C/micro-porous polymer blend electrolyte/LiSr<sub>0.25</sub>Mn<sub>1.75</sub>O<sub>4</sub> was assembled in a dry box under argon atmosphere. The charge–discharge studies were performed at C/10 rate and with the cut-off voltages as 4.5 and 3.0 V for the upper and lower limits, respectively, to prevent the decomposition of polymer electrolyte.

## 3. Results and discussion

### 3.1. X-ray diffraction studies

In order to investigate the influence of various concentrations of Li-salt on polymer blend film, XRD studies were performed on various micro-porous polymer films soaked in 1 M LiClO<sub>4</sub>, 2 M LiClO<sub>4</sub>, 3 M LiClO<sub>4</sub>, 4 M LiClO<sub>4</sub> and 5 M LiClO<sub>4</sub> electrolyte solutions. But only the X-ray diffraction patterns of PVdF-co-HFP-PAN based micro-porous polymer films soaked in 4 M LiClO<sub>4</sub> and 5 M LiClO<sub>4</sub> solutions are given in Fig. 1(a and b). It can be seen from Fig. 1(a) that a decrease in relative intensity with broadening of the apparent peak was observed when compared with other complexes. This may create interaction between the salt–plasticizer, plasticizer–polymer and salt–polymer, which results in the micro-porous gel polymer electrolyte with lower crystallinity with rich amorphous phase which is manifested by the broad diffraction peak centered at 2θ = 20.40°. Further increase in salt concentration (5 M LiClO<sub>4</sub>) increases the relative intensity of diffractogram peak due to undissociation of LiClO<sub>4</sub> salt (Fig. 1(b)) which is manifested by the broad diffraction peak centered at 2θ = 19.00°. Thus, the X-ray diffraction studies reveal the complex formation in the polymer matrices.

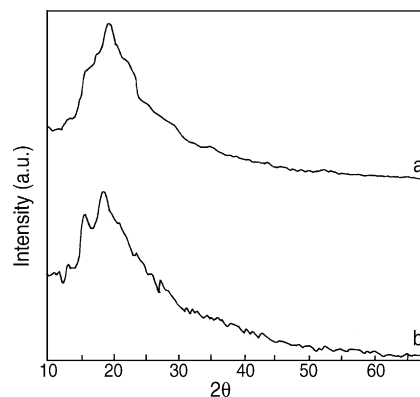


Fig. 1. X-ray diffraction patterns for micro-porous polymer film soaked in: (a) 4 M and (b) 5 M LiClO<sub>4</sub> electrolyte solution.

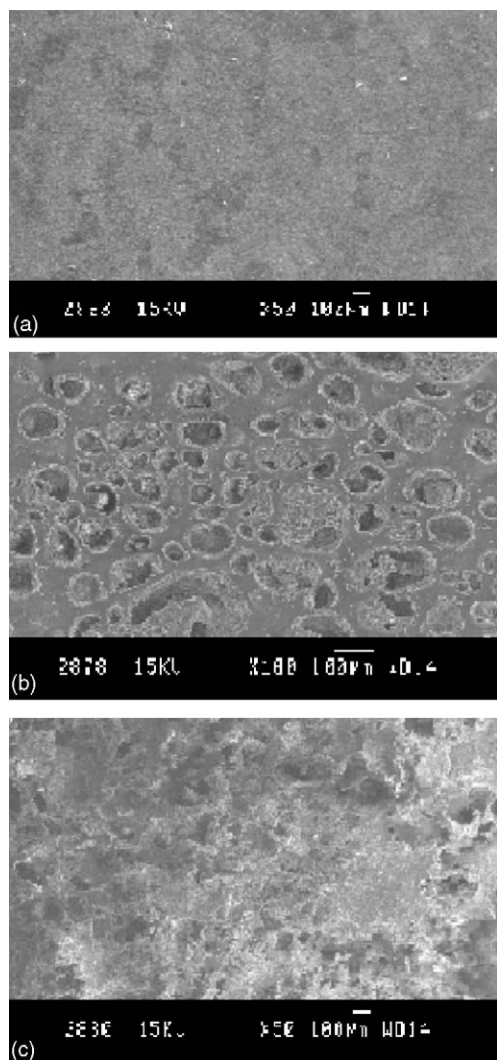


Fig. 2. SEM photographs for PVdF-HFP/PAN based: (a) polymer film, (b) micro-porous polymer membrane and (c) micro-porous polymer electrolyte.

### 3.2. SEM studies

Fig. 2(a–c) shows scanning electron micrographs of PVdF-*co*-HFP-PAN based polymer blend film and micro-porous polymer blend film of high ionic conductivity, before and after soaking in 4 M LiClO<sub>4</sub> electrolyte solution. It can be seen from Fig. 2(a) that the complete miscibility of the PVdF-*co*-HFP-PAN based polymer blend film with no pores and voids. After phase inversion process, the polymer blend film has large voids and cavities of almost uniform size as shown in Fig. 2(b). Hence, the uptake of electrolyte solution by this polymer membrane is higher than the conventional polymer film and the phase separation could also be observed in the micro-porous polymer membrane when it is impregnated in the electrolyte solution which is evident from Fig. 2(c). During this soaking process, PAN is swelled in preference to PVdF-*co*-HFP, and therefore, the immobilization of PVdF-*co*-HFP rich phase followed by the phase separation occurred. This PVdF-*co*-HFP rich phase pulls the liquid electrolyte in

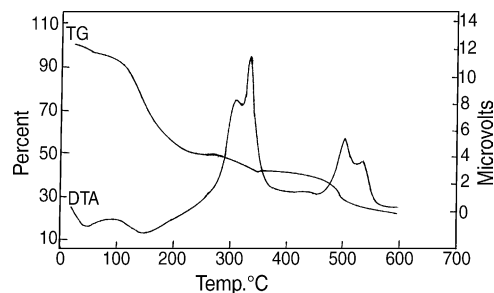


Fig. 3. TG/DTA curves for micro-porous polymer electrolyte of high ionic conductivity.

the course of phase separation. Hence, the liquid electrolyte contact with PVdF-*co*-HFP rich phase is much lower than the PAN rich phase.

### 3.3. Thermal studies

The thermal stability of the polymer electrolyte is also an important parameter to guarantee acceptable performances in lithium batteries. Fig. 3 shows the TG/DTA curve of micro-porous polymer blend electrolyte of high ionic conductivity system. The TG curve reveals that the sample starts to lose its mass at the temperature below 148.17 °C. This initial loss is due to the evaporation of residual solvent and the transition of the electrolyte film and the volatilization of monomers and oligomers adsorbed in the matrix can also be responsible for this initial mass loss [13]. It is also observed that the transition has occurred at 128.57 °C with a weight loss of 20% followed by the first decomposition which takes place at 161.90 °C with gradual weight loss of about 33.63%. Beyond this temperature, there is a rapid weight loss of 57% upto 340.20 °C. Complete decomposition of the film takes place between 467.85 and 571.42 °C with corresponding weight loss of about 61.88 and 80%, respectively.

In the DTA curve, two endothermic peaks were observed at 371.42 and 519.04 °C followed by four exothermic peaks at 312.46, 335.16, 504.26 and 533.96 °C, respectively. The first decomposition temperature occurs in the range of 207–361.90 °C, and it is accompanied by two large exothermic peaks at 312.46 and 335.16 °C followed by two exothermic peaks at 504.26 and 533.96 °C, respectively, with an appreciable weight loss of about 76.87%. This indicates the complete decomposition of the polymer electrolyte film, which is in good agreement with the TG curve. From, the above discussion, it is concluded that the thermal stability limit of the micro-porous polymer blend electrolyte is 161.90 °C.

### 3.4. Conductivity studies

The ionic conductivity of micro-porous PVdF-*co*-HFP-PAN based polymer blend electrolytes was measured with an intention of finding the part played by PAN in the blend. Hence, the ionic conductivities of the (PVdF-*co*-HFP-PAN)

Table 1  
Conductivity data of micro-porous polymer electrolyte at room temperature

Serial number	PVdF-HFP (%)	PAN (%)	Conductivity ( $\text{S cm}^{-1}$ )
1	100	0	$1.52 \times 10^{-3}$
2	90	10	$1.67 \times 10^{-3}$
3	80	20	$1.78 \times 10^{-3}$
4	70	30	$1.86 \times 10^{-3}$
5	60	40	$1.92 \times 10^{-3}$
6	50	50	$2.02 \times 10^{-3}$

Table 2  
Ionic conductivity values of micro-porous polymer membrane soaked in different concentrations of  $\text{LiClO}_4$  electrolyte solution at various temperatures

Concentration	Ionic conductivity $\times 10^{-3}$ ( $\text{S cm}^{-1}$ )					
	298 K	313 K	323 K	333 K	343 K	353 K
1 M $\text{LiClO}_4$	2.02	3.12	4.63	5.80	6.59	7.91
2 M $\text{LiClO}_4$	2.46	3.72	4.90	6.14	7.36	8.63
3 M $\text{LiClO}_4$	2.73	3.94	5.17	6.95	8.94	9.01
4 M $\text{LiClO}_4$	3.41	4.27	5.76	7.14	9.13	9.70
5 M $\text{LiClO}_4$	3.37	4.01	5.24	6.99	9.09	9.43

micro-porous polymer blend electrolyte were measured by varying the content of the blend in various proportions and are given in Table 1. From Table 1, it can be seen that the micro-porous polymer blend electrolyte has two conductive phases: one is the swollen polymer chain, and the other is the liquid electrolyte in the cavities and also increase in PAN content in the PVdF-co-HFP matrix increases the conductivity due to the higher intake of the electrolyte solution.

Also, the variation of ionic conductivity has been analyzed by varying the electrolyte salt concentrations keeping the (PVdF-co-HFP-PAN) blend ratio constant at different temperatures in between 25 and 80 °C (Table 2). It can be seen from Table 2 that the ionic conductivity of micro-porous polymer blend electrolyte depends on the concentration of the conductivity species and their mobility. The effect of lithium salt concentrations in the polymer matrix on logarithmic scale conductivity is shown in Fig. 4. It can be seen from the Fig. 4 that the ionic conductivity increases with increase in Li-salt concentration upto 4 M  $\text{LiClO}_4$  and it was

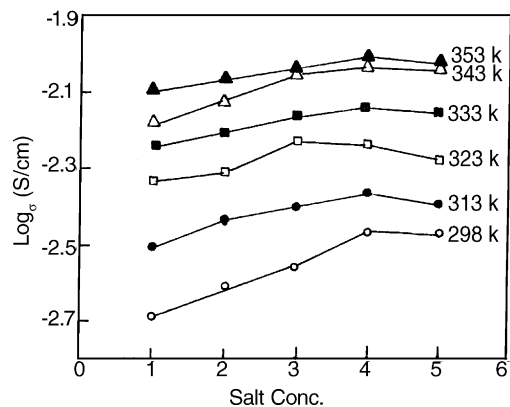


Fig. 4. Dependence of ionic conductivity on salt concentration for micro-porous polymer electrolyte at various temperatures.

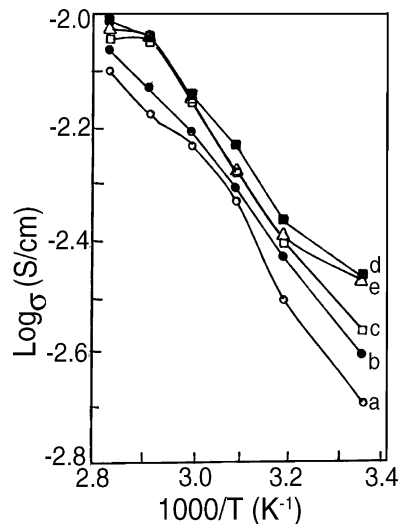


Fig. 5. Arrhenius plot of micro-porous polymer electrolyte for different salt concentrations: (a) 1 M, (b) 2 M, (c) 3 M, (d) 4 M and (e) 5 M  $\text{LiClO}_4$ .

found to be  $3.41 \times 10^{-3} \text{ S cm}^{-1}$ . This value is higher than the PVdF-co-HFP-PEO system [14]. Beyond this concentration, the ionic conductivity decreases. This is due to undissociation of Li-salt and the formation of ion-pairs and ion-triplet, which cause constraint in the polymer segmental motion and also increases the crystallinity nature of polymer electrolyte. The conductivity also increases with increase in temperature for all concentrations [15]. Hence, the polymer electrolyte obeys the VTF relation. It is due to the amorphous nature of micro-porous polymer blend electrolyte which facilitates the fast Li-ion motion in the polymer network, and it also provides a higher free volume on increasing the temperature [16].

Fig. 5 shows the Arrhenius plot for micro-porous polymer blend electrolyte as a function of Li-salt concentration using an optimum (PVdF-co-HFP-PAN) blend ratio. It can be seen from the figure that the non-linear nature of plots suggest that the increase in temperature increases the ionic conductivity is due to an inverse in ionic mobility and also segmental mobility of the polymer chain that will assist fast ion-transport which may prevent the formation of ion cloud.

### 3.5. Electrochemical stability

Generally, the current–voltage study of the polymer electrolyte has been employed to determine whether the polymer electrolyte can withstand the operating voltage of the battery system or not by linear sweep voltammetry and its corresponding voltammogram as shown in Fig. 6. It can be observed from the voltammogram that the anodic decomposition limit of the polymer electrolyte can be considered as the voltage at which the current flows through the cell. The observed anodic stability of micro-porous polymer electrolyte is upto 4.8 V versus  $\text{Li/Li}^+$ . Hence, the polymer electrolyte may have good compatibility with high-voltage electrode materials.

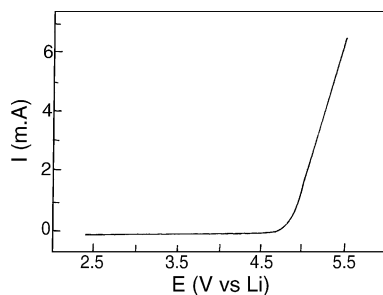


Fig. 6. Linear sweep voltammogram curve of micro-porous polymer electrolyte of high ionic conductivity.

Table 3

Transference number of micro-porous polymer membrane soaked in different concentrations of  $\text{LiClO}_4$  electrolyte solution

Concentration	Transference number
1 M $\text{LiClO}_4$	0.624
2 M $\text{LiClO}_4$	0.682
3 M $\text{LiClO}_4$	0.701
4 M $\text{LiClO}_4$	0.782
5 M $\text{LiClO}_4$	0.761

### 3.6. Transference number

In the dc-potentiostatic polarization of the Li/micro-porous polymer blend electrolyte interface, a constant potential of 10 mV was applied to the symmetrical Li/micro-porous polymer blend electrolyte/Li cell, and the current flowing through the cell was recorded as a function of time. The transference number of  $\text{Li}^+$  ion in micro-porous polymer blend membrane soaked in different concentrations of  $\text{LiClO}_4$  electrolyte solution is given in Table 3, and a representative dc-polarization curve of micro-porous polymer blend film soaked in 4 M  $\text{LiClO}_4$  electrolyte solution is shown in Fig. 7. Its corresponding ac-impedance spectrum is obtained before and after dc-polarization measurements with an applied potential difference of 10 mV. It can be seen from the polarization curve that the initial current rises up ( $I_0$ ) and is 21.64  $\mu\text{A}$  and after the long time of polarization, a steady state current is established at a much lower level ( $I_s$ ) and is 16.92  $\mu\text{A}$  within about 1.41 h and its corresponding ac-

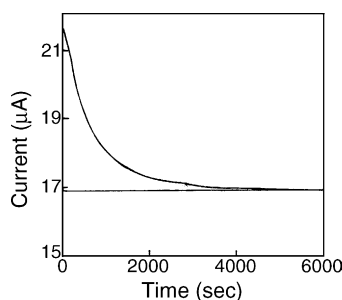


Fig. 7. dc-polarization curve of micro-porous polymer electrolyte of high ionic conductivity.

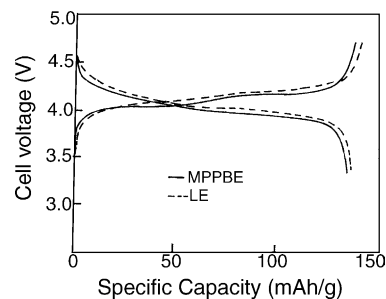


Fig. 8. Charge and discharge curve of micro-porous polymer electrolyte film of high ionic conductivity.

impedance value such as  $R_b^0$ ,  $R_b^s$ ,  $R_i^0$  and  $R_i^s$  are 7.02, 9.84, 72.14 and 129.07  $\Omega$ , respectively, which gives the transference number ( $T^+$ ) ca. 0.782. It reveals that both interfacial and bulk resistance did not change significantly during the dc-potential polarization studies, which may be due to the unique stability between the lithium electrode and the polymer electrolyte interface.

### 3.7. Charge–discharge studies

The charge–discharge curve of carbon/micro-porous polymer blend electrolyte / $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  cell is shown in Fig. 8. It is obvious that the cell at the C/10 rate achieves a capacity of 135  $\text{mAh g}^{-1}$ . By comparison of the discharge curves of micro-porous polymer electrolyte with liquid electrolyte, the specific capacity of micro-porous polymer blend electrolyte is almost equal to that of liquid electrolyte.

## 4. Conclusion

The PVdF-co-HFP-PAN based micro-porous polymer blend electrolyte can be prepared by a phase inversion technique. The conductivity of PVdF-co-HFP based micro-porous polymer blend electrolyte was influenced by increase in PAN content and concentration of  $\text{LiClO}_4$ . It obeys the Arrhenius plot of conductivity and also the VTF relation. The PVdF-co-HFP-PAN based micro-porous polymer blend electrolyte has the highest ionic conductivity of  $3.41 \times 10^{-3} \text{ S cm}^{-1}$  at 25  $^\circ\text{C}$ . It has thermal stability upto 161.90  $^\circ\text{C}$  and its anodic decomposition voltage is 4.82 V versus  $\text{Li/Li}^+$ . Since it depends on concentrations and types of salt and solvents, etc., the decomposition voltage may be extended to higher voltage, the transference number of PVdF-co-HFP-PAN based micro-porous polymer blend electrolytes is 0.782, which is higher than that of a PEO or PAN or PMMA or PVdF-co-HFP alone based gel polymer electrolyte and also increases the specific capacity of the cathode materials. This value is almost the same as that of liquid electrolytes. Hence, PVdF-co-HFP-PAN based micro-porous polymer blend electrolytes are good candidates for high-voltage rechargeable lithium batteries.

## Acknowledgements

The authors gratefully acknowledge the DST, New Delhi for the financial support.

## References

- [1] J.M. Tarascon, A.S. Goetz, C. Schmutz, F. Shokoohi, P.C. Warren, *Solid State Ionics* 86–88 (1996) 46.
- [2] T. Michot, A. Nishimoto, M. Watanabe, *Electrochim. Acta* 45 (2000) 1347.
- [3] H. Huang, S. Lowunder, *J. Electrochem. Soc.* 148 (2001) A279.
- [4] A. Magistris, P. Mustarelli, E. Quastarone, P. Piaggio, A. Bottino, *Electrochim. Acta* 46 (2001) 1635.
- [5] D.W. Kim, K.A. Noh, J.H. Chan, S.H. Kim, J.M. Ko, *Solid State Ionics* 144 (2001) 329.
- [6] J.M. Tarascon, A.S. Goetz, C. Schmutz, F. Shokoohi, P.C. Warren, *Solid State Ionics* 86–88 (1996) 49.
- [7] C. Lampe-onnerud, P. Culver, A. Pupasquier, J.A. Shelburne, I. Plitz, A.S. Goetz, J.M. Tarascon, *Proceedings of 15th International Seminar and Exchange on Primary and Secondary Batteries*, Fort Lauderdale, FL, March 1998.
- [8] D. Peramunage, D.M. Pasquariello, K.M. Abraham, *J. Electrochem. Soc.* 142 (1995) 1789.
- [9] A. Manuel Stephen, D. Teeters, *Electrochim. Acta* 48 (2003) 2143.
- [10] A. Magistris, P. Mustarelli, E. Quartarone, P. Piaggio, *Electrochim. Acta* 46 (2001) 1635.
- [11] K.M. Abraham, Z. Jiang, B. Carroll, *Chem. Mater.* 9 (1997) 1978.
- [12] J. Evans, C.A. Vincent, P.G. Bruce, *Polymer* 28 (1987) 2324.
- [13] V. Mano, M.I. Felisbersti, T. Matencio, M.A. Depaoli, *Polymer* 37 (1996) 5165.
- [14] H. Wang, H. Huang, S.L. Wunder, *J. Electrochem. Soc.* 147 (2000) 2853.
- [15] M.B. Armand, J.M. Chabagno, J.N. Mundy (Eds.), *Fast-Ion Transport in Solid*, North-Holland, Amsterdam, 1979, p. 131.
- [16] M. Rater, D.F. Shriver, *Chem. Rev.* 88 (1988) 109.