

Short communication

# Investigation of electrical and electrochemical properties of PVDF-based polymer electrolytes

N.S. Mohamed<sup>a</sup>, A.K. Arof<sup>b,\*</sup>

<sup>a</sup> Centre for Foundation Studies in Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

<sup>b</sup> Physics Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

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## Abstract

A study has been made of the electrical and electrochemical characteristics of polyvinylidene fluoride (PVDF)-based polymer electrolytes. The room-temperature ionic conductivity of PVDF increases by up to four orders of magnitude on addition of trifluoromethane sulfone ( $\text{LiCF}_3\text{SO}_3$ ), and a further increase is observed with the incorporation of an ethylene carbonate (EC) plasticizer. The conductive behavior of the electrolytes over a wide temperature range ( $-100$  to  $100^\circ\text{C}$ ) is examined. An electrochemical cell has been fabricated using the film that gives the highest ionic conductivity at room temperature. The discharge characteristics of cells stored/heated at different temperatures have been studied in the 4.2–2.5 V voltage range. A greater discharge capacity is delivered on heating. In general, the discharge capacity and the capacity retention increase with the increase in temperature. This can be attributed to a reduction in the interfacial resistance due to an improvement in the electrolyte|electrode interfacial adhesion.

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## 1. Introduction

Lithium-ion batteries with lithiated metal oxide for the positive electrode (cathodes) and carbon for the negative electrode (anode) have been finding use in many electronic applications with current drains that range from a few microamperes (e.g., memory back-up, real-time clock) to many milliamperes (e.g., laptop computers and hand phones) [1,2]. It has been found that the performance of a lithium-ion battery depends strongly on the type of electrode and electrolyte materials used.

Polymer-based electrolyte materials have been reported as promising materials for use in secondary lithium batteries due to their unique properties such as high ionic conductivity, ability to provide good electrode|electrolyte contact, and physical flexibility [3,4]. The use of solid polymer electrolytes can avoid problems associated with liquid electrolytes such as leakage and gas formation that arises from solvent decomposition. This leads to improvement in battery design [5]. Solid polymer batteries constructed with only thin-film electrodes and electrolytes can be made to be very compact, lightweight and highly reliable.

There have been many efforts to synthesize polymer electrolytes with high conductivities at room temperature for use in rechargeable lithium batteries. For example, polyvinylidene fluoride (PVDF)-based polymer electrolytes have been widely studied [6–12]. This is because PVDF has a high dielectric constant ( $\epsilon = 8.4$ ) for a polymer, which should assist in greater ionization of the lithium salt to provide a high concentration of charge carriers. Furthermore, polymer electrolytes based on PVDF are expected to be highly stable at positive potentials due to the strongly electron-withdrawing functional group ( $-\text{C}-\text{F}$ ) [5,6]. In this work, an investigation is made of the electrical and electrochemical properties of PVDF-based polymer electrolytes. The conductive behavior is studied by impedance spectroscopy over a wide range of temperature, from  $-100$  to  $100^\circ\text{C}$ . In order to investigate the electrochemical properties of the PVDF-based electrolytes, cells with the configuration  $\text{LiCoO}_2|\text{polymer electrolyte}|\text{MCMB}$  are fabricated.

## 2. Experimental

### 2.1. Preparation and characterization of polymer electrolytes

The PVDF-based polymer electrolyte films were prepared by the solution-casting technique. The conductivity of the

\* Corresponding author. Tel.: +60-3-7967-4085; fax: +60-3-7967-4146.  
E-mail address: [akarof@um.edu.my](mailto:akarof@um.edu.my) (A.K. Arof).

polymer electrolyte was determined by impedance spectroscopy in a frequency range from 42 Hz to 1 MHz by means of a 3512 Hi Tester analyzer that was interfaced to a computer for data acquisition.

## 2.2. Cell fabrication and characterization

The cathode was prepared by mixing lithium cobalt oxide ( $\text{LiCoO}_2$ ) and activated carbon into a paste. The paste was then cast on to an aluminum mesh, which was coated with activated carbon for better electrical contact. The anode was prepared in a similar manner and used meso carbon micro beads (MCMB) as the active material. This material was cast on to a copper mesh.

The electrochemical cells were assembled by sandwiching the PVDF polymer electrolyte between the anode and the cathode materials. The square-shaped cells were then sealed in a metallized plastic bag. The sealing process was performed in an argon-filled glove-box (MBRAUN lab master 130-TP 170). The cells were tested with a galvanostat (Arbin MSTAT4) that was interfaced to a computer.

## 3. Results and discussion

### 3.1. Characteristics of PVDF-based polymer electrolytes

The variation of room-temperature conductivity with the doping salt content in the PVDF-based electrolytes is presented in Fig. 1. The conductivity increases as the amount of  $\text{LiCF}_3\text{SO}_3$  added to the PVDF increases. The addition of this salt increases the ionic conductivity by up to four orders of magnitude. The best conductivity is given by the PVDF electrolyte system that contains 25 wt.%  $\text{LiCF}_3\text{SO}_3$ . In order to study the effect of ethylene carbonate (EC) on the conductivity, plasticized PVDF– $\text{LiCF}_3\text{SO}_3$  systems were

prepared. This was achieved by adding various amounts of EC to the system that gave the highest conductivity. The addition of EC improves the conductivity to a maximum value of  $4.30 \times 10^{-4} \text{ S cm}^{-1}$  for the system that contains 30 wt.% EC, see Fig. 1(b). The conductivity tends to decline with further addition of EC.

Plots of the dielectric constant as a function of frequency at room temperature for pure PVDF and for the unplasticized and plasticized PVDF– $\text{LiCF}_3\text{SO}_3$  systems with the highest conductivity are shown in Fig. 2. The latter two systems report higher values of the dielectric constant at a given frequency, particularly at low frequencies. Therefore, it can be inferred that the increase in conductivity observed in Fig. 1 can be attributed to an increase in the number of ions [13]. The addition of EC to PVDF– $\text{LiCF}_3\text{SO}_3$  complexes is expected to increase the degree of salt dissociation and thus produce more ions. On the other hand, the decrease of conductivity for a system that contains a high salt or plasticizer content could be due to the association of ions or a decrease in the mobility of ions, as described by Rajendran et al. [14].

The ionic conductivity at various temperatures for pure PVDF and the unplasticized and plasticized PVDF– $\text{LiCF}_3\text{SO}_3$  system with the highest conductivity are presented in Fig. 3. The data show that the conductivity of pure PVDF increases gradually in the  $1000/T$  range from 5.5 to 3.0, which corresponds to a temperature range of  $\sim -90$  to  $60^\circ\text{C}$ . The conductivities of the PVDF– $\text{LiCF}_3\text{SO}_3$  and EC plasticized PVDF– $\text{LiCF}_3\text{SO}_3$  systems increase linearly over the  $1000/T$  range of  $\geq 4.9$  which corresponds to temperatures  $\leq -70^\circ\text{C}$ . The dependence of the dielectric constant on frequency at various temperatures for the highest conducting EC plasticized system is given in Fig. 4. The dielectric constant at a particular frequency appears to increase with temperature. This suggests an increasing content of ‘free’ ions. Corresponding plots for pure PVDF and PVDF– $\text{LiCF}_3\text{SO}_3$  exhibit

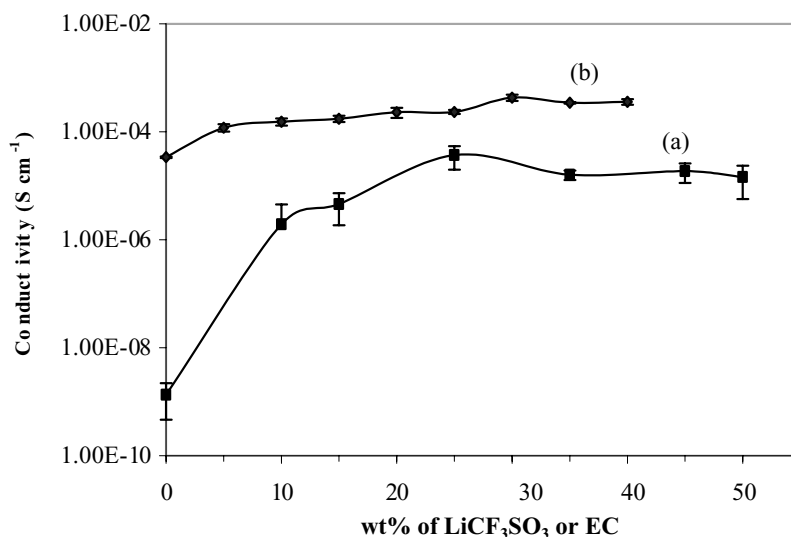


Fig. 1. Variation of conductivity with (a) salt and (b) EC contents.

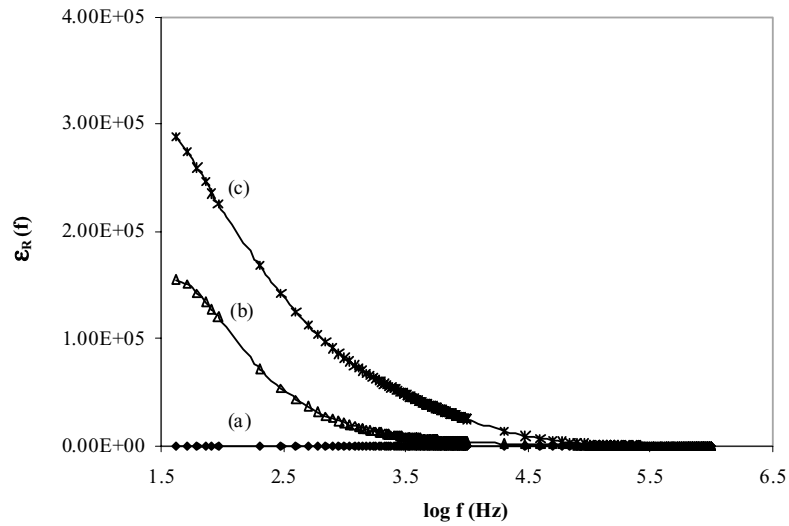


Fig. 2. Dielectric constant as a function of frequency for: (a) pure PVDF; (b) highest conducting PVDF–LiCF<sub>3</sub>SO<sub>3</sub> system; and (c) highest conducting EC plasticized PVDF–LiCF<sub>3</sub>SO<sub>3</sub> system.

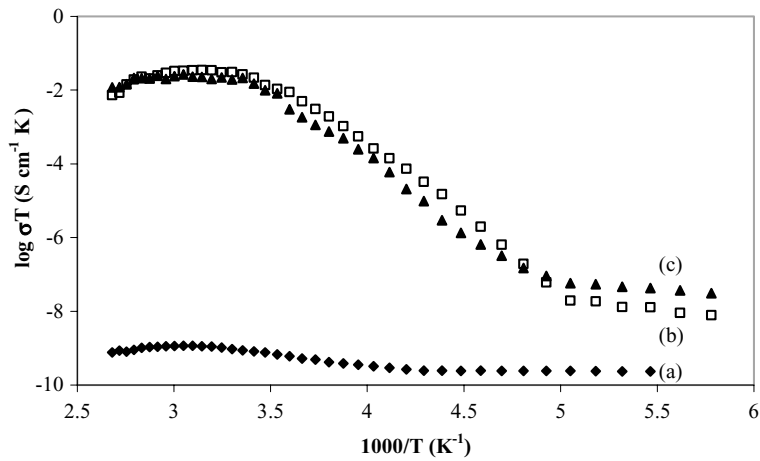


Fig. 3. Variation of  $\log \sigma T$  with temperature for: (a) pure PVDF; (b) highest conducting PVDF–LiCF<sub>3</sub>SO<sub>3</sub> system; and (c) highest conducting EC plasticized PVDF–LiCF<sub>3</sub>SO<sub>3</sub> system.

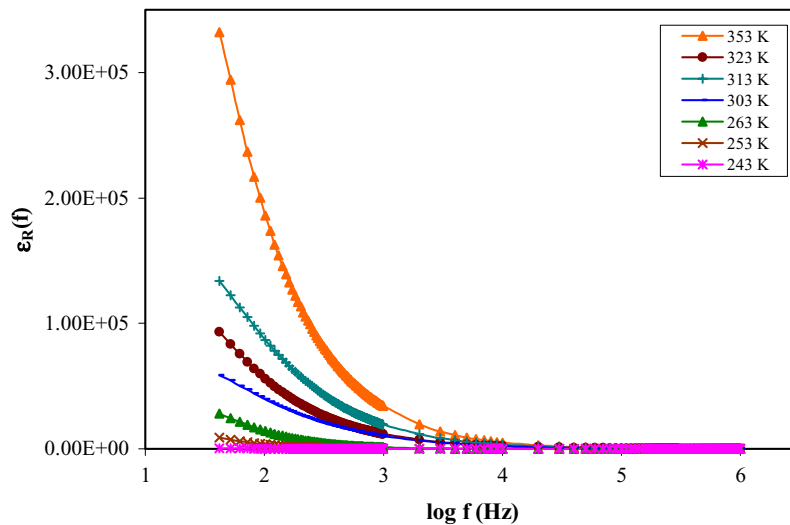


Fig. 4. Variation of dielectric constant with temperature for highest conducting EC plasticized PVDF–LiCF<sub>3</sub>SO<sub>3</sub> system.

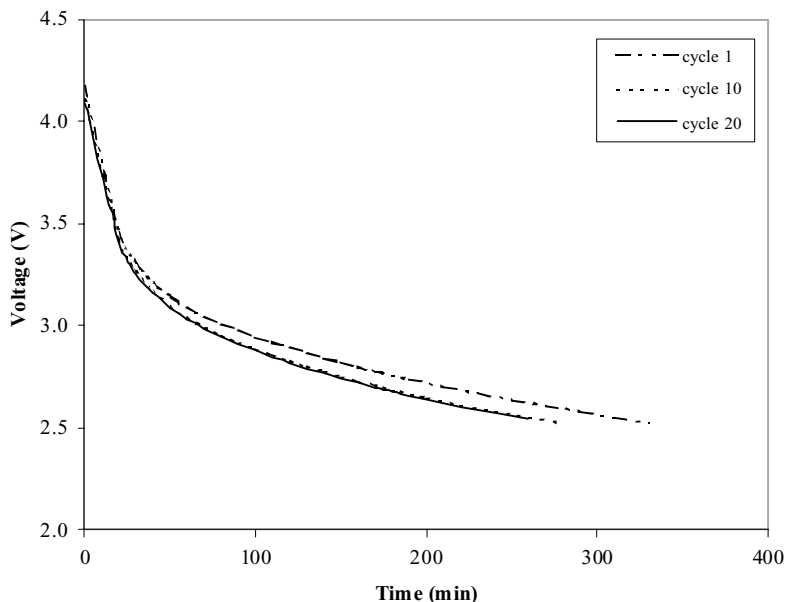


Fig. 5. Discharge profiles of unheated PVDF-based cell.

the same trend. Therefore, the increase in conductivity with temperature observed in Fig. 3 can be attributed to an increase in ‘free’ ion concentration. This could be due to an increase in the degree of salt dissociation, and in the degree of re-dissociation of ion aggregates, as a result of temperature increase. The abrupt change in slope at  $1000/T \simeq 5.0$  ( $\sim -73^\circ\text{C}$ ) for the PVDF– $\text{LiCF}_3\text{SO}_3$  and EC plasticized PVDF– $\text{LiCF}_3\text{SO}_3$  systems corresponds to the  $\gamma$ -relaxation of PVDF, as described by Kalfoglou and Williams [15]. Those authors used the spectra of loss modulus and loss tangent versus temperature to show that the  $\gamma$ -relaxation of PVDF occurs at  $\sim -80^\circ\text{C}$ , i.e., close to the value reported here.

### 3.2. Characteristics of PVDF lithium ion cells

Battery application commonly requires an ionic conductivity above  $0.1 \text{ mS cm}^{-1}$  [16]. Since the highest conducting electrolyte film investigated in this study shows a conductivity value of about  $0.3 \text{ mS cm}^{-1}$ , it can be considered as a suitable candidate for use in batteries or electrochemical cells. In order to evaluate the electrochemical performance of lithium-ion polymer cells that employ the PVDF-based polymer electrolytes, a cell with the configuration of  $\text{LiCoO}_2|\text{PVDF electrolyte}|\text{MCMB}$  was fabricated. The cell was subjected to ‘conditioning’ prior to charge–discharge characterization. The latter was undertaken in the 2.5 and

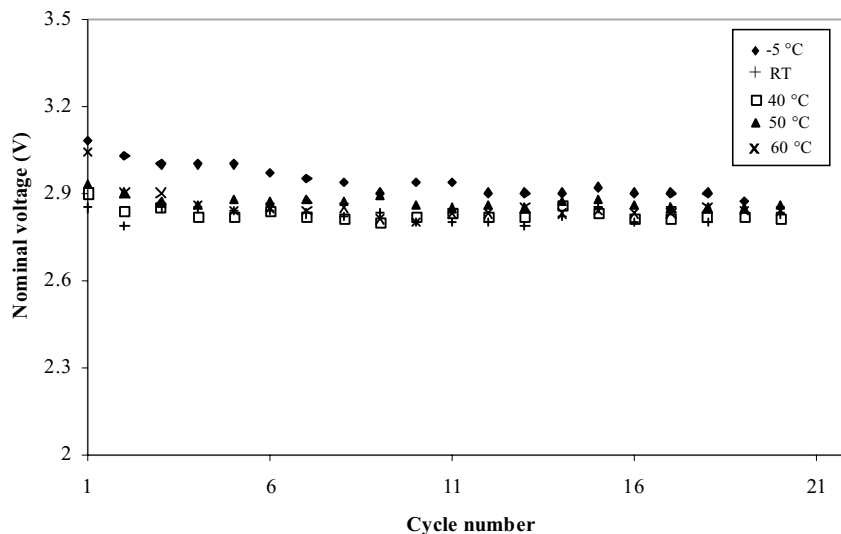


Fig. 6. Nominal voltage vs. cycle number for PVDF-based cells stored/heated at different temperatures.

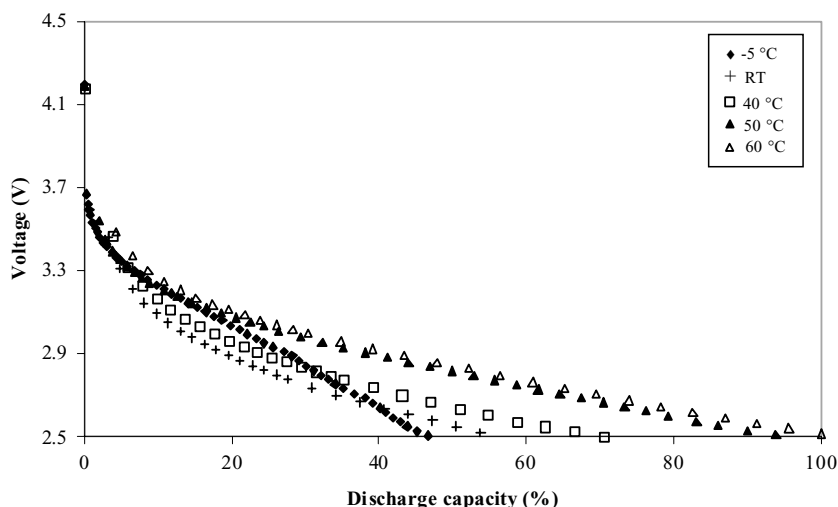


Fig. 7. Voltage vs. initial discharge capacity (with reference to discharge capacity of cell heated at 60 °C) of cells stored/heated at different temperatures.

4.2 V range with charge and discharge currents of 10 and 1 mA, respectively. The effect of temperature on discharge capacity was also examined. For this purpose, the cells were stored/heated at  $-5$ , 40, 50 and 60 °C for 4 h and then tested.

Charge–discharge profiles for the cell at room temperature are presented in Fig. 5. It is seen that the discharge time decreases with cycling. This implies that the capacity of the cell decreases upon cycling. The capacity decline can be related mainly to the increase of interfacial resistance of the LiCoO<sub>2</sub> electrolyte, as described by other workers [17–19]. Nominal voltage–cycle number plots for PVDF-based cells heated/stored at different temperatures are presented in Fig. 6. The nominal voltage of the cell stored at room temperature shows a slight decline over the first three cycles, but stabilizes at  $\sim 2.9$  V on further cycling. Plots for cells stored/heated at different temperatures, i.e.,  $-5$ , 40, 50 and 60 °C, follow the same trend.

The discharge capacities of cells stored/heated at different temperatures as a percentage of the discharge capacity of a cell heated at 60 °C are shown in Fig. 7. The low capacities of cells heated below 60 °C could be due to the low diffusivity of lithium ions in the solid polymer electrolyte [20]. The performance of a cell can be influenced by the resistance of the electrolyte [18]. A polymer electrolyte with a thick film ( $\sim 500$   $\mu\text{m}$ ) will have a larger resistance than separators normally used in cells that employ liquid electrolyte ( $\sim 25$   $\mu\text{m}$ ), and this may have an adverse effect on the discharge capacity of the cell. After heat treatment at 40 °C, the cell delivers a discharge capacity that is  $\sim 3\%$  higher than the value obtained at room temperature. It is also interesting to note that higher capacities are obtained on treatment at higher temperatures, i.e., increases of  $\sim 5$  and  $\sim 8\%$  after treatment at 50 and 60 °C, respectively. The discharge capacity delivered by the cell after storage at  $-5$  °C is about  $\sim 2\%$  less than the capacity at room temperature, or  $\sim 50\%$

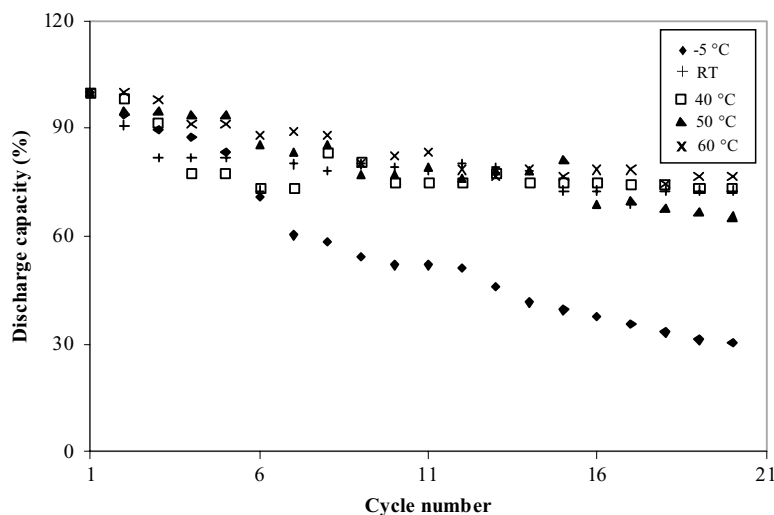


Fig. 8. Discharge capacity (with reference to initial discharge capacity) as a function of cycle number for cells stored/heated at different temperatures.

less than the capacity that is obtained when the cell is heated to 60 °C. A higher discharge capacity at 80 °C has been obtained [20] for a Li|LiCoO<sub>2</sub> cell that used an electrolyte based on a polyethylene glycol diacrylate (PEGDA)–PVDF blend. These workers also found that the capacity at –4 °C was 15% less than that delivered at room temperature. The low capacity of the cell stored at –5 °C in the work reported here can be attributed to depletion of lithium ions at the electrolyte|electrode interface, as described by Song et al. [20].

Discharge capacity as a function of cycle number for cells stored/heated at different temperatures is shown in Fig. 8. Clearly, cells exhibit greater discharge capacity after being heat-treated. At the 20th cycle, cells heated at 40 and 60 °C retain about 70–80% of the initial discharge capacity, respectively. This demonstrates that heat treatment has a considerable effect on cell performance. A feasible explanation can be found by considering the interface resistance, which is influenced by the adhesiveness of the polymer electrolyte [21]. At room temperature, the interfacial adhesion could be low and thus give rise to a high interfacial resistance. It is likely that the adhesiveness of the electrolyte is improved by heat treatment. This leads to a decrease in interfacial resistance and, consequently, raises the discharge performance. Heating the cell at higher temperatures may result in further enhancement of the interfacial adhesion and in further reduction of the interfacial resistance. This would explain why the cell shows the best performance after being heated at 60 °C.

#### 4. Conclusions

An enhancement of the ionic conductivity of PVDF-based polymer electrolytes by up to five orders of magnitude has been achieved by the incorporation of an EC plasticizer. Accordingly, the EC plasticized PVDF–LiCF<sub>3</sub>SO<sub>3</sub> polymer electrolytes show sufficient ionic conductivity for use as separators in lithium-ion cells. At this stage, however, the conductivity and other characteristics, such as adhesiveness,

porosity and thickness, of the polymer electrolytes have not been optimized. Thus, there is scope for further improvements in the performance of cells that use the polymer electrolytes that have been fabricated in this study.

#### References

- [1] S. Megahead, M. Ebner, *J. Power Sources* 54 (1995) 155.
- [2] R.M. Dell, *Solid State Ionics* 134 (2000) 139.
- [3] F.B. Dias, P. Lambertus, J.B.J. Velchuis, *J. Power Sources* 88 (2000) 169.
- [4] S.S. Sekhon, M. Deepa, S.A. Agnihotry, *Solid State Ionics* 136–137 (2000) 1189.
- [5] J. Song, Y.Y. Wang, C.C. Wun, *J. Power Sources* 77 (1999) 183.
- [6] H.S. Choe, J. Giacci, M. Alamgir, K.M. Abraham, *Electrochim. Acta* 40 (1995) 228.
- [7] F. Croce, G.B. Appetecchi, S. Slane, M. Solomon, M. Taverez, S. Arumugam, Y. Wang, S. Greenbaum, *Solid State Ionics* 86–88 (1996) 307.
- [8] Z. Jiang, B. Carroll, K.M. Abraham, *Electrochim. Acta* 42 (17) (1997) 2667.
- [9] M.M.E. Jacob, A.K. Arof, *Electrochim. Acta* 45 (2000) 1701.
- [10] E. Tsuchida, H. Ohno, K. Tsunemi, *Electrochim. Acta* 28 (5) (1983) 591.
- [11] K. Tsunemi, H. Ohno, E. Tsuchida, *Electrochim. Acta* 28 (6) (1983) 833.
- [12] H.-C. (Alex) Shiao, D. Chua, H.P. Lin, M. Solomon, *J. Power Sources* 87 (2000) 167.
- [13] Z. Osman, Z.A. Ibrahim, A.K. Arof, *Carbohydr. Polym.* 44 (2001) 167.
- [14] S. Rajendran, O. Mahendran, R. Kannan, *Mater. Chem. Phys.* 74 (2002) 52.
- [15] N.K. Kalfoglou, H.L. Williams, *J. Polym. Sci.* 17 (1973) 3367.
- [16] R. Koksang, I.I. Olsen, D. Shackel, *Solid State Ionics* 69 (1994) 320.
- [17] D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, B.N. Popov, *J. Power Sources* 91 (2000) 122.
- [18] M.G.S.R. Thomas, P.G. Bruce, J.B. Goodenough, *J. Electrochem. Soc.* 132 (1985) 1521.
- [19] D. Aurbach, M.D. Levi, E. Levi, H. Teller, B. Markovsky, G. Salitra, U. Heider, L. Heider, *J. Electrochem. Soc.* 145 (1998) 3024.
- [20] M.K. Song, J.Y. Cho, B.W. Cho, H.W. Rhee, *J. Power Sources* 110 (2002) 209.
- [21] D.W. Kim, J.M. Ko, J.H. Chun, *J. Power Sources* 93 (2001) 151.