

## Optimisation of PVdF-based polymer electrolytes

N. Muniyandi, N. Kalaiselvi, P. Periyasamy, R. Thirunakaran\*, B. Ramesh babu,  
S. Gopukumar, T. Premkumar, N.G. Renganathan, M. Raghavan

Central Electrochemical Research Institute, Karaikudi 630 006, Tamilnadu, India

Received 9 January 2001; accepted 12 January 2001

### Abstract

An attempt was made to synthesise PVdF-based polymer electrolytes containing 1:1 EC:PC plasticiser in various salts such as LiAsF<sub>6</sub>, LiPF<sub>6</sub> and LiBF<sub>4</sub> at different ratios using PVdF as homopolymer. Though, having a high ionic conductivity, certain films were found to be fragile, an indication of poor mechanical strength. Therefore, PVdF–PVC blend polymers were prepared using different ratios of PVdF–PVC as well as with different amounts of plasticiser mixture. Film characterisation was attempted using XRD, DSC, impedance and conductivity measurements. A particular combination of PVdF–PVC in the ratio 25:5 was observed to have high ionic conductivity and good mechanical strength. The electrochemical stability and the stability of lithium–polymer interface of the prepared polymer electrolytes were checked in terms of charge–discharge and impedance studies. Effect of storage time and cyclability are discussed. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Electrolytes/PVdF–PVC polymer; PVdF polymer; Ionic conductivity

### 1. Introduction

With the advent of lithium-ion battery technology [1], aiming for higher output voltages became the next target to be hit in the field of rechargeable lithium batteries.

However, further development of lithium-ion batteries paved the way for the entry of lithium-ion conducting polymer electrolytes in which the conventional non-aqueous electrolyte is immobilised by a polymer matrix [2]. Different polymer matrices and processes are proposed in the literature [3–6]. The concept of gel electrolytes with a high ionic conductivity and mechanical strength came in to existence as early as 1975s [7–9]. In this regard, host polymers for the gel electrolytes, such as poly acrylonitrile [10,11], poly methylmethacrylate [9,10], poly ethylene oxide [12], poly vinylidene fluoride [13] and a co-polymer of vinylidene fluoride with hexa fluoro propylene (PVdF–HFP) [14–17] have been identified as promising cathodes, because they possess high ionic conductivity and good stability.

Of late, PVdF as homopolymer and related co-polymers or blends of PVdF-based polymer electrolytes are gaining popularity, because of their high degree of flexibility, added to other meritorious properties viz. high room temperature conductivity, dimensional stability etc.

In this paper, polymer film electrolytes were made up of PVdF homopolymer and a blend of PVdF–PVC with a range of lithium salts viz. LiAsF<sub>6</sub>, LiPF<sub>6</sub> or LiBF<sub>4</sub> and using EC + PC as a common plasticiser. Optimisation of these polymer electrolytes were carried out in terms of the amount of polymer, plasticiser and the quantity of lithium salt required to prepare polymer films of sufficient mechanical strength and conductivity.

### 2. Experimental

#### 2.1. Preparation of PVdF gel electrolyte films

A mixture of PVdF (Aldrich, average molecular weight ca. 5,340,000), high purity EC + PC (1:1) and the lithium salt (LiBF<sub>4</sub> or LiPF<sub>6</sub> or LiAsF<sub>6</sub>) was heated in order to cast the film with the required properties. EC (Merck-Schuchardt) and PC (Fluka AG) were distilled using the usual procedures and kept under an argon atmosphere.

In detail, the calculated amount of a 1:1 mixture of EC + PC and the respective lithium salt such as LiBF<sub>4</sub> (Merck-Schuchardt), LiPF<sub>6</sub> (Across Organics) or LiAsF<sub>6</sub> (Merck-Schuchardt) were weighed individually into a Pyrex bottles. An appropriate amount of PVdF in tetrahydrofuran (THF) was heated to 160–175°C with stirring for 1 h to ensure complete dissolution. To the hot solution, was added

\* Corresponding author.

E-mail address: rthirunakaran@usda.net (R. Thirunakaran).

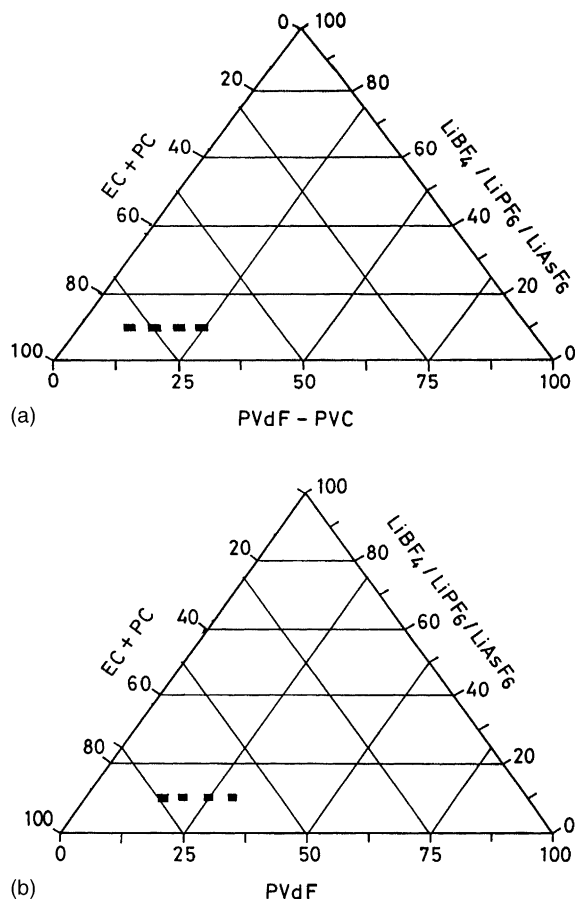


Fig. 1. Composition diagrams of: (a) PVdF–EC + PC–Li salts (lower); (b) PVdF:PVC–EC + PC–Li salts (upper).

the mixture of plasticiser (EC + PC) and the corresponding lithium salt. The solution was further heated with continued stirring to get an homogenous and viscous solution. The resultant viscous solution was poured over glass plates and adjusted for uniform thickness using doctor blades. The cast film was dried in a vacuum oven at 50°C for about 24 h. Solvent free stable films of uniform thickness (100 µm) were obtained, which were characterised later.

Fig. 1a shows the range of compositions that were prepared.

## 2.2. Preparation of PVdF–PVC blend electrolyte films

A similar procedure was adopted. To the polymer mix of selected ratios of PVdF–PVC, individual lithium salts (LiAsF<sub>6</sub>, LiPF<sub>6</sub> or LiBF<sub>4</sub>) were added with 1:1 EC + PC as a common plasticiser. The films were dried in a vacuum oven at 50°C for 24 h and all the films were then found to be stable and solvent free.

Fig. 1b shows the range of compositions that were prepared.

## 2.3. Preparation of composite cathode

High purity LiCoO<sub>2</sub>, graphite and the gel polymer electrolyte, containing plasticiser and lithium salt, were mixed in

65:10:25 ratio under hot conditions and blended thoroughly. The paste was coated over aluminium foil, the thickness adjusted to 75 µm and dried in a vacuum oven at 110°C for 24 h.

## 2.4. Characterisation studies

The free-standing films were subjected to X-ray diffraction analysis using a Jeol 8030 X-ray diffractometer with a nickel filtered Cu K $\alpha$  radiation.

Thermal stabilities of PVdF powder and the resultant PVdF-based polymer electrolytes were studied using differential scanning calorimetry (DSC–SEIKO, TA Station SSC–5000 series). The samples were heated at 300°C from room temperature at a rate of 10°C min<sup>-1</sup>.

Conductivity measurements were made on an electrochemical impedance analyser (EG&G PAAR, model no. 263 A, lock in amplifier, model no. 5210). The conductivity of the polymer films was measured using a two-electrode cell configuration, constructed from a brass body housing, 20 mm in diameter stainless steel electrodes. The electrodes were screwed into the cell, sandwiching the polymer film between them. The fully assembled cell was connected for room temperature conductivity measurements. The impedance spectrum was obtained using test cells fabricated with the polymer films against lithium metal on both the sides. The impedance spectrum was run between the frequency range of 1 Hz–100 kHz at room temperature and the corresponding Nyquist plots were recorded.

Charge–discharge studies were carried out with a test cell containing a Li/polymer electrolyte/composite LiCoO<sub>2</sub> cathode assembly at room temperature using a constant current of 0.1 mA. The electrochemical interface stability of the polymer electrolytes were measured as a function of impedance over a range of storage periods.

## 3. Results and discussion

The polymer electrolyte films which had been prepared were examined for homogeneity, stability and ease of preparation.

### 3.1. Dimensional stability

The dimensional stabilities observed from the PVdF films are given in Table 1. From the table, it is evident that the higher polymer content is required to get dimensionally stable PVdF films. Though homogeneity was observed invariably for all the ratios, the films with >25% of PVdF were found to be better, based on the stability point of view. Generally, viscosity of the electrolyte depends upon the weight ratio of polymer, plasticiser and the lithium salt [14]. Evidently, the viscosity of the polymer electrolytes involved in the present investigation favours the addition of the lowest possible amount of lithium salt to have the

Table 1  
Dimensional stability of PVdF polymer electrolyte films

Name	PVdF:EC + PC:Li salt	Condition
PVdF (BF <sub>4</sub> )	20:70:10	Fragile
	25:65:10	Fragile
	30:60:10	Stable
	35:55:10	Stable
PVdF (PF <sub>6</sub> )	20:70:10	Fragile
	25:65:10	Fragile
	30:60:10	Stable
	35:55:10	Stable
PVdF (AsF <sub>6</sub> )	20:70:10	Fragile
	25:65:10	Fragile
	30:60:10	Stable
	35:55:10	Stable

optimum viscosity for the formation as well as the free-standing nature of the polymer film.

The amount of lithium salt to be added has been carried out as a separate study and the results will be published elsewhere [18]. Based upon the results of the study, the concentration of lithium salts was fixed as 10% throughout, irrespective of the nature of the salt added and the type of polymer material employed. Subsequently, gel polymer electrolytes containing 30 and 35% polymer along with 10% LiBF<sub>4</sub> or LiPF<sub>6</sub> or LiAsF<sub>6</sub> were identified for good dimensional stability, homogeneity and free standing nature of the film.

A similar analysis was carried out on PVdF–PVC electrolytes, see Table 2. These were also found to be interesting, as all the films cast with 2.5–10% PVC in the blend along with 20–27.5% PVdF were found to be dimensionally stable but the ratio 15:15 (PVdF:PVC) was found to be brittle (Table 2). Thus, the optimisation of polymer electrolytes can be summarised as: an addition of 30–35% PVdF for a homopolymer and an addition of 20–27.5% PVdF with 2.5–10% PVC for PVdF–PVC blend polymer electrolyte is recommended from the dimensional stability standpoint.

Table 2  
Dimensional stability of PVdF–PVC polymer electrolyte films

File name	PVdF	PVC	EC + PC	Li salt	Condition
PVdF–PVC (BF <sub>4</sub> )	15	15	60	10	Brittle
	20	10	60	10	Free-standing
	25	5	60	10	Free-standing
	27.5	2.5	60	10	Free-standing
PVdF–PVC (PF <sub>6</sub> )	15	15	60	10	Brittle
	20	10	60	10	Free-standing
	25	5	60	10	Free-standing
	27.5	2.5	60	10	Free-standing
PVdF–PVC (AsF <sub>6</sub> )	15	15	60	10	Brittle
	20	10	60	10	Free-standing
	25	5	60	10	Free-standing
	27.5	2.5	60	10	Free-standing

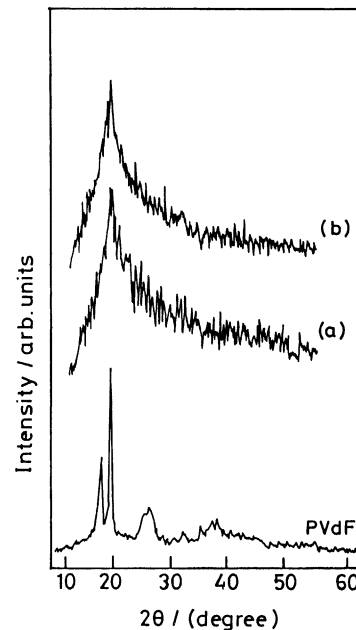


Fig. 2. X-ray diffraction patterns for: (a) 30% PVdF–60% EC + PC–10% LiAsF<sub>6</sub> film; (b) 35% PVdF–55% EC + PC–10% LiAsF<sub>6</sub> film.

### 3.2. X-ray diffraction

X-ray diffraction studies were carried out on the stable films and the results observed are shown in Fig. 2.

XRD patterns of the composition, 30% PVdF, 60% EC + PC, 10% lithium salt and that of 35% PVdF, 55% EC + PC, 10% lithium salt are shown in Fig. 2a and b, respectively.

PVdF, which is highly crystalline by nature, has been modified into the amorphous form in the gel electrolyte, due to the addition of EC + PC and lithium salts. The addition of plasticiser and lithium salt has definitely induced significant disorder into the polymer structure giving a polymer electrolyte of much lower crystallinity [19], which is quite obvious from the broad diffraction peak centred at  $2\theta = 19.8^\circ$ . This is evidence that the polymers apparently undergo structural reorganisation, caused by the swelling process due to the addition of plasticiser and lithium salt.

Similarly, the broad peak centred at  $2\theta = 20.2^\circ$  for PVdF–PVC blend electrolytes (Fig. 3) also confirmed the intimately bound polymer matrix, which has homogeneity and amorphicity, caused mainly by the plasticiser addition. Among the three blended electrolytes, the degree of amorphicity was found to be better for 25:5 and 20:10 ratio of PVdF–PVC than for the 27.5:2.5 ratio.

### 3.3. Differential scanning calorimetry

The DSC data of PVdF and PVdF–PVC blend polymer electrolytes are reproduced in Figs. 4 and 5. An exothermic peak observed between 150–175°C corresponds to the melting point of PVdF. However, the broad exothermic peaks

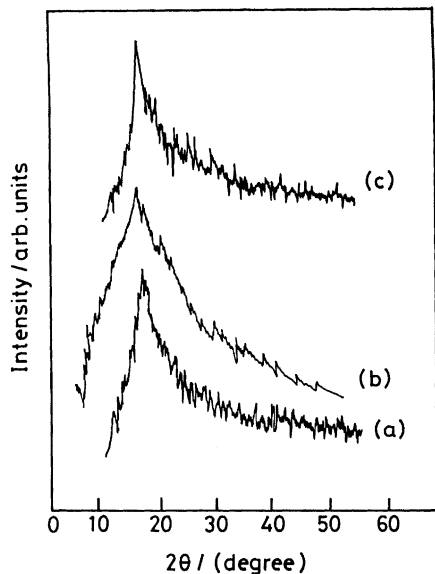


Fig. 3. X-ray diffraction patterns for: (a) 20:10% PVdF:PVC–60% EC + PC–10% LiAsF<sub>6</sub> film; (b) 25:5% PVdF:PVC–60% EC + PC–10% LiAsF<sub>6</sub> film; (c) 27.5:2.5% PVdF:PVC–60% EC + PC–10% LiAsF<sub>6</sub> film.

corresponding to the boiling points of EC and PC are not found in either of the types of polymer electrolytes, an indication that the disappearance of the phase transition of EC + PC is due to the formation of segments of polymer chain (14). Also, the polymer electrolytes exhibited a broad peak at a slightly elevated temperature, which is in favour of the formation of segments of polymer chain with lithium salts resulted from the swelling induced by the addition of

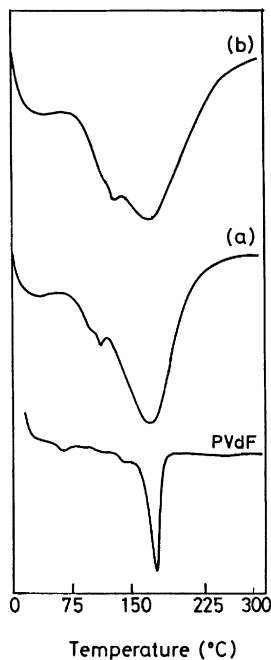


Fig. 4. Differential scanning calorimetry curves of: (a) 30% PVdF–60% EC + PC–10% LiAsF<sub>6</sub> film; (b) 35% PVdF–55% EC + PC–10% LiAsF<sub>6</sub> film.

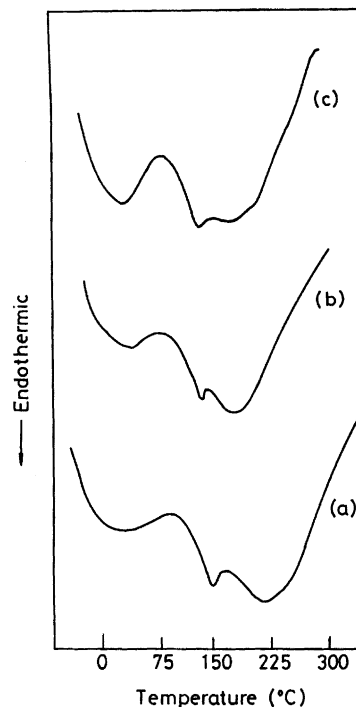


Fig. 5. Differential scanning calorimetry curves of: (a) 20:10% PVdF:PVC–60% EC + PC–10% LiAsF<sub>6</sub> film; (b) 25:5% PVdF:PVC–60% EC + PC–10% LiAsF<sub>6</sub> film; (c) 27.5:2.5% PVdF:PVC–60% EC + PC–10% LiAsF<sub>6</sub> film.

60% EC + PC. Thus, the crystallinity of PVdF has been reduced very much by an optimal addition of 60% EC + PC in both the PVdF and PVdF–PVC blend type of polymer electrolytes.

### 3.4. Electrical conductivity

The conductivity data for the PVdF and the PVdF–PVC electrolytes are summarised in Table 3. Conductivity of the polymer electrolytes, which is determined as a function of weight ratio of polymer to plasticiser, favours the addition of a lesser amount of polymer material. On the other hand, a higher value of the weight ratio increases the mechanical strength, lowers the mobility of charge carriers and results in the reduced conductivity of the polymer electrolytes. Therefore, a combination of a slightly lower amount of polymer and a slightly higher amount of plasticiser are expected to give better results as far as conductivity measurements are concerned. Interestingly, the observed values of conductivity of both PVdF and the blend type PVdF–PVC polymer electrolytes are in good agreement with the expected trend, i.e. among the two stable PVdF polymer electrolyte films, the one due to 30% PVdF with 60% EC + PC showed better conductivity than the film made up of 35% PVdF with 55% EC + PC. However, the other two films viz. 20 and 25% PVdF were not taken in to consideration for conductivity measurements, as they were found to be fragile in nature.

Similarly, among the dimensionally stable PVdF–PVC polymer films, the one with 25:5 ratio of PVdF–PVC with

Table 3  
Room temperature conductivity of some PVdF and PVdF-PVC polymer electrolytes<sup>a</sup>

Sample	PVdF	PVC	EC + PC	Li salt	Conductivity (S cm <sup>-1</sup> )
1	30	–	60	10 (LiBF <sub>4</sub> )	0.00034
2	35	–	55	10 (LiBF <sub>4</sub> )	0.00029
3	30	–	60	10 (LiPF <sub>6</sub> )	0.00047
4	35	–	55	10 (LiPF <sub>6</sub> )	0.00040
5	30	–	60	10 (LiAsF <sub>6</sub> )	0.00066
6	35	–	55	10 (LiAsF <sub>6</sub> )	0.00059
1'	20	10	60	10 (LiBF <sub>4</sub> )	0.00028
2'	25	5	60	10 (LiBF <sub>4</sub> )	0.00040
3'	27.5	2.5	60	10 (LiBF <sub>4</sub> )	0.00034
4'	20	10	60	10 (LiPF <sub>6</sub> )	0.00048
5'	25	5	60	10 (LiPF <sub>6</sub> )	0.00060
6'	27.5	2.5	60	10 (LiPF <sub>6</sub> )	0.00056
7'	20	10	60	10 (LiAsF <sub>6</sub> )	0.00062
8'	25	5	60	10 (LiAsF <sub>6</sub> )	0.00086
9'	27.5	2.5	60	10 (LiAsF <sub>6</sub> )	0.00080

<sup>a</sup> Compositions expressed as weight percents.

60% EC + PC was found to exhibit higher conductivity, irrespective of the type of the lithium salt used. Although, addition of increasing amounts of PVC increases the mechanical stability, it reduces the conductivity values. This is quite obvious from the brittle nature of the 15:15 PVdF-PVC film and the lower conductivity values of 20:10 PVdF-PVC with respect to the 27.5:2.5 and 25:5% PVdF-PVC films. However, the conductivity of the polymer electrolyte with 27.5:2.5 PVdF-PVC is slightly less than the conductivity of 25:5 PVdF-PVC electrolyte, which may be correlated to the less amorphicity of the former with respect to the latter. Also, LiAsF<sub>6</sub> was found to exhibit the maximum conductivity rather than LiBF<sub>4</sub> or LiPF<sub>6</sub>, irrespective of the nature of the polymer and the amount of plasticiser used.

### 3.5. Impedance studies

The passivation that occurs at the lithium interface in the gel polymer electrolytes has been studied by monitoring the impedance behaviour of a symmetrical cell that was kept on open circuit for various periods i.e. 24, 72 h and 1 week. A gradual increase in the impedance values was noted (Fig. 6a and b) which is in accordance with the model proposed by Alamgir and Abraham [5]. It is seen from the figures that the  $R_b$  value remains below 5 k $\Omega$ , during the entire period of storage, thus accounts for the prolonged stability of the polymer. However, the increase in  $R_f$  value noted for both the PVdF and PVdF-PVC polymer electrolytes can be correlated to the growth of passivation film formed due to the reaction of lithium with the polymer electrolyte.

### 3.6. Charge-discharge studies

Electrochemical characterisation with charge-discharge studies were performed using a test cell containing lithium

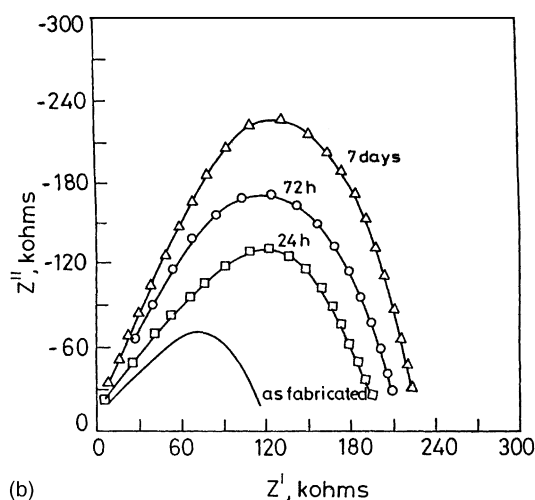
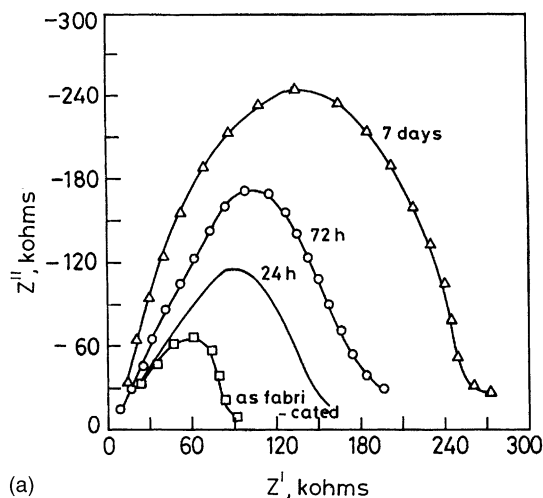


Fig. 6. (a) Impedance changes after storage of Li/PVdF/Li cells; (b) impedance changes after storage of Li/PVdF-PVC/Li cells.

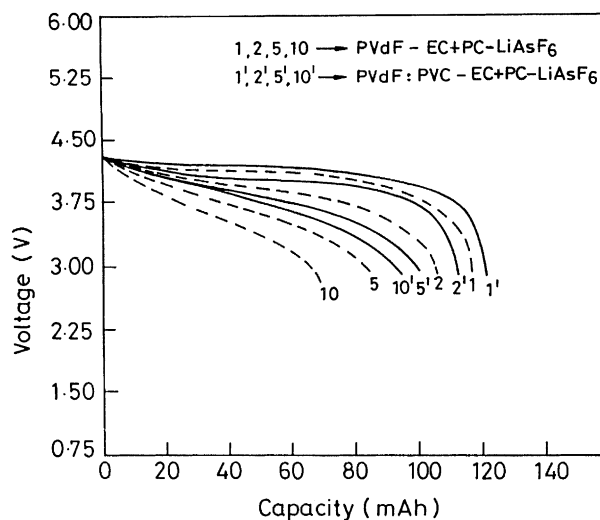


Fig. 7. Discharges from 1st, 2nd, 5th and 10th cycle of a Li/polymer electrolyte/LiCo<sub>2</sub> cell.

as anode, a composite  $\text{LiCoO}_2$  as cathode and the prepared polymer electrolytes of both types. The charge–discharge efficiency agrees with the better retention of capacity of both PVdF and PVdF–PVC types of polymer electrolytes found during cycling. An efficiency of not less than 60% was observed for PVdF electrolytes and an efficiency of around 70% was maintained by the PVdF–PVC blend type of electrolytes (Fig. 7) after 10 cycles. Similarly, the impedance of the as fabricated cells (Li/polymer electrolyte/ $\text{LiCoO}_2$ ) and the cells after 1, 5 and 10 cycles are shown in Fig. 8a and b.

The decrease in impedance with cycling supports the supposition that the passivating film (formed due to the reaction of lithium with the polymer electrolyte) is being removed and thereby the surface of lithium is subsequently

being renewed. These preliminary observations suggest that PVdF–PVC blend polymer electrolytes seem to be more promising than the homopolymer PVdF electrolytes.

#### 4. Conclusions

Homopolymers-containing PVdF require 30–35% of polymer to get a solvent free film of sufficient stability. Alternatively, a combination of 25% PVdF with 5% PVC along with 20 or 27.5% PVdF with 10 and 2.5% PVC, respectively gave better formation of films. Among the stable films of both the categories, films with 60% EC + PC favoured better conductivity, lower resistance and higher thermal stability. Similarly,  $\text{LiAsF}_6$  gave better results than  $\text{LiBF}_4$  and  $\text{LiPF}_6$ , irrespective of the nature of the polymer and the amount of plasticiser used for casting the films.

A combination of 30% PVdF with 60% EC + PC and 10%  $\text{LiAsF}_6$  and 25:5 (PVdF–PVC) with 60% EC + PC and 10%  $\text{LiAsF}_6$  performed better than the rest of the films.

PVdF–PVC blend polymer electrolytes exhibited improved cycling behaviour rather than the PVdF polymer electrolytes.

#### References

- [1] J.M. Tarascon, D. Guyomard, *Electrochim. Acta* 38 (1993) 1221.
- [2] O. Bohnke, G. Frand, M. Rezzazzi, C. Rousselot, C. Truche, *Solid State Ionics* 66 (1993) 105.
- [3] R. Koksang, I.I. Olsen, D. Shackle, *Solid State Ionics* 66 (1994) 320.
- [4] F. Croce, F. Gerace, G. Dautzemberg, C. Passerini, G.B. Appetecchi, B. Scrosati, *Electrochim. Acta* 39 (1994) 2187.
- [5] M. Alamgir, K.M. Abraham, *J. Power Sources* 54 (1995) 40.
- [6] A.S. Gozdz, C.N. Schmutz, J.M. Tarascon, P.C. Warren, U.S. Patent no. 5418091, May 1995.
- [7] G. Feuillade, P. Perche, *J. Appl. Electro. Chem.* 5 (1975) 63.
- [8] K.M. Abraham, M. Alamgir, *J. Electrochem. Soc.* 137 (1990) 1657.
- [9] G.B. Appetecchi, F. Croce, B. Scrosati, *Electrochim. Acta* 40 (1995) 991.
- [10] S. Kakuda, T. Momma, T. Osaka, G.B. Appetecchi, B. Scrosati, *J. Electrochem. Soc.* 142 (1995) L1.
- [11] T. Osaka, T. Momma, H. Ito, B. Scrosati, *J. Power Sources* 68 (1997) 392.
- [12] T. Osaka, T. Homma, T. Momma, H. Yarimizu, *J. Electroanal. Chem.* 421 (1997) 153.
- [13] F. Boudin, X. Andrieu, C. Jehoulet, I.I. Olsen, *J. Power Sources* 81/82 (1999) 804.
- [14] Z. Jiang, B. Carroll, K.M. Abraham, *Electrochim. Acta* 42 (1992) 2667.
- [15] J.M. Tarascon, C.N. Schmutz, A.S. Gozdz, P.C. Warren, F. Shokoohi, M R S Fall Meeting Proc. 595–604 (1994) 369.
- [16] A.S. Gozdz, C.N. Schmutz, J.M. Tarascon, U.S. Patent no. 5, 1994, pp. 296–318.
- [17] J. Fuller, A.C. Breda, R.T. Carlin, *J. Electrochem. Soc.* 144 (1999) L67.
- [18] N. Kalaiselvi, P. Periyasamy, R. Thirunakaran, B. Ramesh babu, N.G. Renganathan, N. Muniyand, *Bull. Mater. Sci.*, in press.
- [19] M. Armand, W. Gorecki, R. Andreani, B. Scrosati, in: *Proceedings of the 2nd International Meeting on Polymer Electrolytes*, Elsevier, New York, 1990, p. 91.

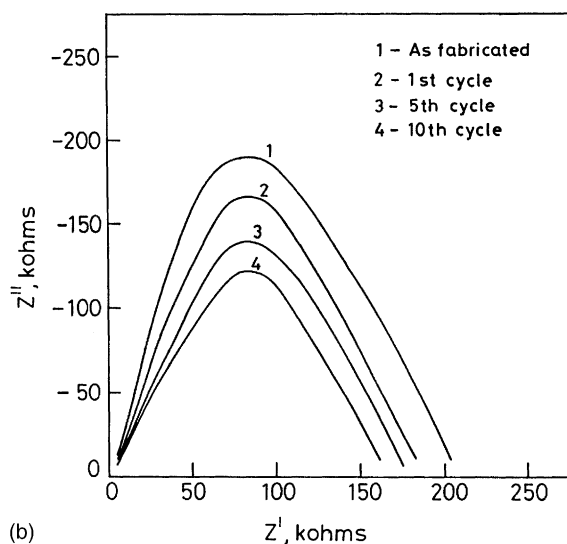
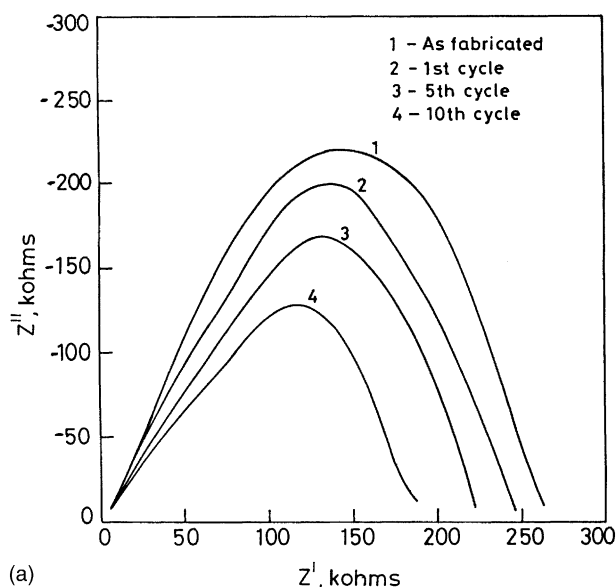


Fig. 8. (a) Variation of impedance with cycle number for a Li/PVdF/ $\text{LiCoO}_2$  cell; (b) variation of impedance with cycle number for a Li/PVdF–PVC/ $\text{LiCoO}_2$  cell.