

Electrochemical studies on [(1 – x)PVA–xPMMA] solid polymer blend electrolytes complexed with LiBF₄

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Abstract

PVA–PMMA-based electrolyte films containing fixed LiBF₄ salt are prepared using solvent casting technique. The complexation has been confirmed from XRD and FTIR spectral studies. The ac impedance studies are performed to evaluate the ionic conductivity of the polymer electrolyte membranes in the range 302–373 K and the temperature dependence seems to obey the VTF relation. The influence of blend compositions on the ionic conductivity has been discussed. The maximum ionic conductivity value for PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ (10 wt.%) system is found to be $2.801 \times 10^{-5} \text{ S cm}^{-1}$ at 302 K. Thermal analysis and CV studies have been performed and reported here.

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1. Introduction

In recent past electrochemical energy storage devices have a tremendous role in technical applications like computers, communication devices, industrial controls, electric vehicles, space ships, laboratory equipments, etc. Moreover they have stringent need in the portable electronic market like solar cells, pacemakers, remote controls and even in toys. In these emerging technologies they are having an exclusive demand for long life, environmentally friendly, low cost, reliable rechargeable batteries with specific energy power as expected [1]. Such power was obtained by using the liquid electrolytes due to its hectically moving charge carriers. On the other hand, to overcome the drawbacks of liquid electrolytes like leakage, reaction with the electrode, poor electrochemical stability, the solid polymer electrolytes are extensively studied in the past decades. Due to its excellent mechanical, thermal stability and high ionic conductiv-

ity solid polymer electrolytes yield the attention of many researchers towards the identification and development of solid polymer electrolytes in optimum number of applications such as computer memory back up, smart windows, photovoltaic cells, fuel cells, electric vehicle traction and space power applications, etc. In order to remain structurally stable during manufacturing, cell assembly and no leakage from cell container, the polymer electrolytes should possess good mechanical stability. To incorporate this stability the polymer blending is one of the most promising ways. When two or more polymers give rise to a homogeneous mixture, miscible or compatible blend is formed in which one polymer is adopted to absorb the electrolytes' active species while another remains as an undissolved, inert second phase providing toughness to the polymer electrolyte films. Also Berthier et al. [2] established that ionic conductivity in polymer electrolytes is associated with amorphous phase of studied samples. Among the various methods to produce high ionic conduction, flexibility, good mechanical strength and amorphous nature, polymer blends are the most promising and feasible approach [3]. The blend-based polymer

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electrolytes are exemplified by many research groups [4,5]. Recently Faria and Moreira [6] reported the kinetics, structure transitions and dielectric behaviour of P(VdF-TrFE)/PMMA blends.

Poly(vinyl alcohol) films have high tensile strength and abrasion resistance; and hence used as binder, electrochemical windows, blood prosthetic devices, fuel cells, double layer capacitors, etc. [7]. Every et al. [8] reported that PVA-based lithium electrolytes have conductivity in the range 10^{-8} to 10^{-4} S cm $^{-1}$. The conductivity of PVA polymer complexes also show high values by blending PVA with other suitable polymer. Poly(methyl methacrylate) (PMMA) was first reported by Iijima et al. [9] and it has good compatible nature. PMMA gels were found to have better interfacial properties towards lithium electrodes [10]. Singh and Singh [11] studied the compatibility of PVA–PMMA polymer blends in solution by both viscometric and ultrasonic techniques. They also reported the interaction parameters of the polymer blend solvent system. In the present study a new polymer electrolyte composed of PVA–PMMA blend as the host polymer and lithium tetrafluoroborate (LiBF $_4$) as the doping salt has been prepared. The salt LiBF $_4$ was chosen since it has low lattice energy [12]. The role of interaction between polymer host on conductivity and phase structure of the blend-based electrolytes are discussed using the results of X-ray diffraction (XRD), Fourier transform-infra red (FTIR) and ac impedance studies. The polymer film with maximum conductivity has been subjected to thermal and cyclic voltammetric (CV) measurements and the results are reported here.

2. Experimental

PVA with an average molecular weight of 115,000 (BDH, England), PMMA with an average molecular weight of 120,000 (Aldrich, USA) and inorganic salt LiBF $_4$ (E-Merck, Germany) were used in the present study. PVA, PMMA and LiBF $_4$ were dried before use, in the Logitech DTC 5050 vacuum oven at 100, 90 and 80 °C, respectively, under 10^{-3} Torr pressure for 10 h. When the melting temperature is nearer to the decomposition of the polymers, solvent casting technique is preferred for casting the films since this process reduces the energy for melting [13]. Here, [(1 – x)PVA–xPMMA–LiBF $_4$

(10 wt.%) polymer electrolytes were prepared (where x = 1, 0.8, 0.6, 0.4, 0.2 and 0) using the solvent casting technique and hereafter the samples were called B1, B2, B3, B4, B5 and B6, respectively, as shown in Table 1 or according to the polymers blend composition (PVA:PMMA) like 0:100, . . . , 60:40, . . . , 100:0.

The above compositions of lithium salt, PVA and PMMA were dissolved separately in distilled DMF (Merck) and mixed together. The resultant solution was stirred and heated continuously at 70 °C for several hours until the mixture gets homogeneous gelly nature. The film was cast by spreading the suspension on glass plate and in the Teflon bushes. Finally the film was dried at 85 °C in the vacuum oven under $\approx 10^{-3}$ Torr pressure for 4–5 h to remove further traces of DMF. The resulting film was visually examined for its dryness and free-standing nature. Chemical storage, film casting and cell assemblies were performed in the vacuum atmosphere. The thickness of the electrolytes was measured using Mitutoyo Digimatic Micrometer and verified by Airwedge method. The thickness of the electrolytes lies in the range from 0.1 to 0.5 mm.

The crystalline structure of the resultant electrolyte films is investigated using XRD. Equipment used in this study was JEOL, JDX 8030 X-ray diffractometer. The fundamental vibrations of the polymer complexes are studied by FTIR analysis made in the range 4000–400 cm $^{-1}$ using a Perkin Elmer 577 IR spectrometer.

The bulk electrical conductivity of the electrolyte was measured using a conductivity jig of SS electrode. The measurements were made with the help of Keithley LCZ meter Model 3330. The conductivity values are evaluated from the complex impedance plots in the temperature range 302–373 K. All the conductivity measurements have been performed under vacuum (10^{-3} Torr).

In order to examine the thermal stability of the electrolyte having higher conductivity value, it is subjected to thermogravimetric/differential thermal analysis (TG/DTA). The STA 1500 PL Thermal Sciences is used in the present study. The sample was put in an Al pan and was heated at a rate of 10 °C min $^{-1}$ up to 700 °C. TG and DTA curves are recorded. To investigate the cyclability and reversibility of the electrolyte film, CV studies have been performed using EG&G Impedance Analyzer Model 6310.

Table 1
Ionic conductivity values of [(1 – x)PVA–xPMMA]–LiBF $_4$ (10 wt.%) system

Sample code	Compositions, x	Conductivity value of [(1 – x)PVA–xPMMA]–LiBF $_4$ (10 wt.%) system ($\times 10^{-5}$ S cm $^{-1}$)							
		302 K	308 K	318 K	328 K	338 K	348 K	358 K	373 K
B1	1.0	0.85	1.17	1.69	2.08	2.58	3.04	3.55	3.63
B2	0.8	1.19	1.51	2.72	3.52	4.37	5.03	5.95	6.73
B3	0.6	1.66	3.14	3.58	3.73	4.99	5.42	7.29	8.45
B4	0.4	2.80	4.68	4.74	5.12	7.83	9.72	10.31	15.46
B5	0.2	1.14	1.79	2.39	3.42	3.82	3.93	4.35	5.15
B6	0	0.89	1.20	1.93	2.85	3.67	3.80	4.11	4.86

3. Results and discussion

3.1. XRD analysis

In order to examine the influence of PMMA contents on the crystalline structure of PVA-based electrolytes, X-ray diffraction studies have been performed for PVA, PMMA, LiBF₄ and the complexes. Fig. 1a–c shows the X-ray diffraction patterns of pure PVA, PMMA and LiBF₄. Fig. 1d–i represents the diffraction patterns of complexes.

The diffraction peaks appearing at $2\theta = 38$ and 44° in LiBF₄ salt are slightly shifted in the complexes. The peaks appearing at $2\theta = 6.5$, 8.2 and 9.3° of pure LiBF₄ salt get disappeared in the complexes. From the diffraction patterns Fig. 1c–i, it is found that there is a decrease in the relative intensity of the peak appearing at 12.3° of pure LiBF₄. This gives a clear indication of complexation of the salt in the polymer complexes. Thus X-ray diffraction analysis reveals that the complexation takes place in the polymer complexes and influence of PMMA content in PVA, LiBF₄ complexes.

3.2. FTIR analysis

Fig. 2a–i shows the IR spectra of PVA, PMMA, LiBF₄ and [(1-x)PVA-xPMMA]-LiBF₄ (10 wt.%) complexes. The O–H (hydroxyl) stretching band in the IR is by far the most characteristic IR band of alcohols and phenols. The free O–H vibration occurs as a sharp peak at 3575 cm^{-1} in pure PVA, but this peak is broadened in the complexes, which is due to hydrogen bond formation. There are few weak absorptions below and above this vibrational frequency which are absent in the complexes. This may be due to the breaking of hydrogen bonding. The broad hydroxyl band in the polymer complexes is displaced towards the lower wave numbers, and it gives a clear indication about the specific interactions in the polymer matrices.

The characteristic vibrational frequency assigned to asymmetric CH₂ stretching and aliphatic C–H stretching occurring at 2925 cm^{-1} in pure PVA is shifted to 2936 cm^{-1} in the PVA-rich complexes. The C=O stretching of unhydrolyzed acetate group at 1725 cm^{-1} is shifted to 1730 cm^{-1} in the PVA-rich complexes [14]. The frequency at 2954 cm^{-1} may be assigned to CH₃ asymmetric stretching of PVA.

The vibrational peaks appearing at 2954 , 1736 cm^{-1} are assigned to CH₃ asymmetric stretching and C=O stretching, respectively. The vibrational bands at 1483 and 1452 cm^{-1} are assigned to CH₂ scissoring and CH₃ asymmetric bending or deformation of PMMA. The characteristic peak at 1389 cm^{-1} is assigned to O–CH₃ deformation of PMMA. The vibrational peaks appearing at 1280 and 874 cm^{-1} are attributed to C–O stretching and C–O–C stretching of PMMA. The vibrational peaks at 1173 , 947 and 750 cm^{-1} may be assigned to CH₂ twisting, wagging and rocking modes of PMMA.

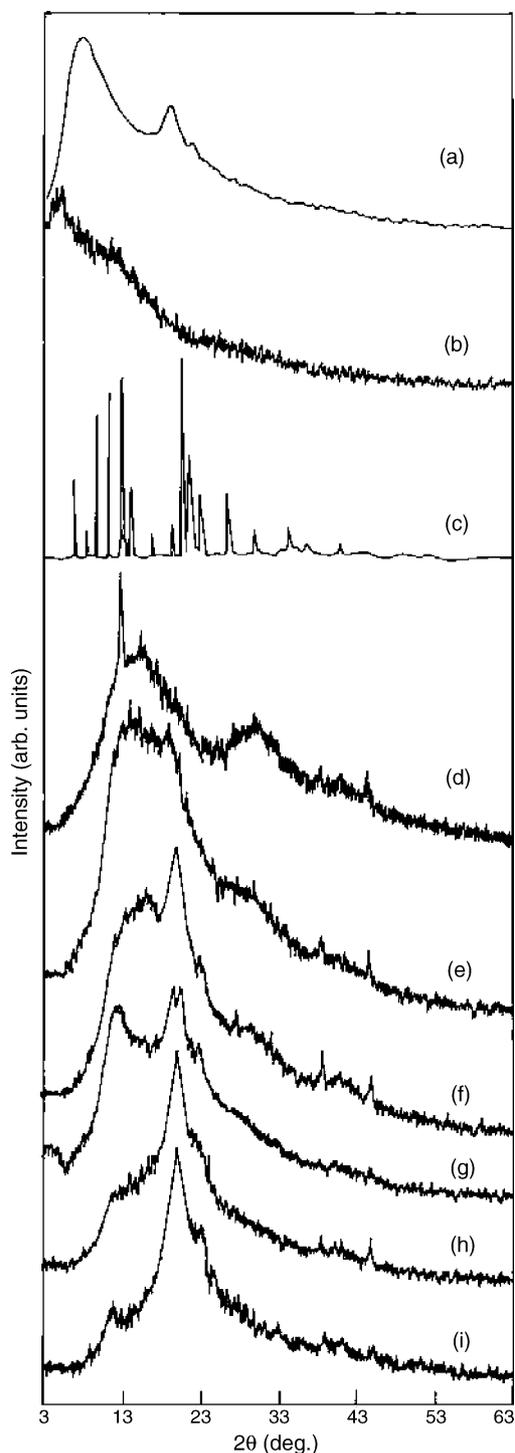


Fig. 1. X-ray diffraction patterns of: (a) PVA; (b) PMMA; (c) LiBF₄; (d) PVA–PMMA (0:100)–LiBF₄ (10 wt.%); (e) PVA–PMMA (20:80)–LiBF₄ (10 wt.%); (f) PVA–PMMA (40:60)–LiBF₄ (10 wt.%); (g) PVA–PMMA (60:40)–LiBF₄ (10 wt.%); (h) PVA–PMMA (80:20)–LiBF₄ (10 wt.%); (i) PVA–PMMA (100:0)–LiBF₄ (10 wt.%).

The characteristic peak at 510 cm^{-1} is attributed to broad band BF₄⁻ bending of LiBF₄ which is shifted to 520 cm^{-1} in all the complexes. From the IR spectra, it is observed that some of the peaks are shifted and some of them

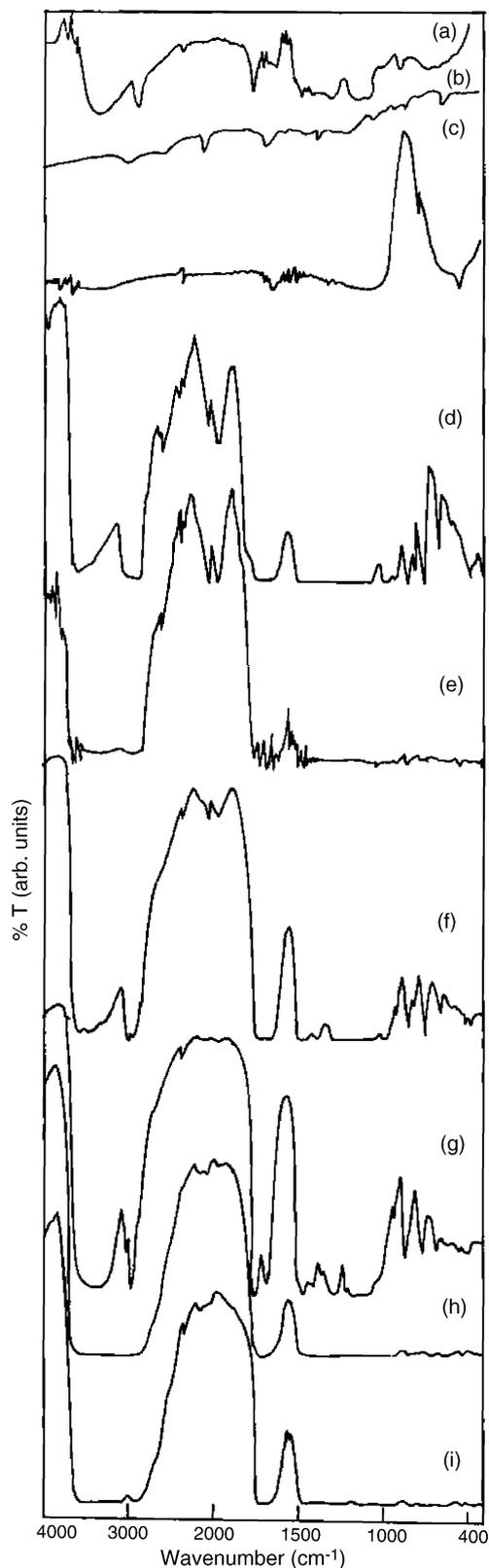


Fig. 2. FTIR spectra of: (a) PVA; (b) PMMA; (c) LiBF_4 ; (d) PVA-PMMA (0:100)- LiBF_4 (10 wt.%); (e) PVA-PMMA (20:80)- LiBF_4 (10 wt.%); (f) PVA-PMMA (40:60)- LiBF_4 (10 wt.%); (g) PVA-PMMA (60:40)- LiBF_4 (10 wt.%); (h) PVA-PMMA (80:20)- LiBF_4 (10 wt.%); (i) PVA-PMMA (100:0)- LiBF_4 (10 wt.%).

are disappeared with respect to the pure compounds. This results manifested the conclusion about the specific interactions in polymer-salt matrices and hence the complexation.

3.3. Conductivity studies

The conductivity is measured by sandwiching the electrolytes between the stainless steel electrodes. The conductivity values of the polymer electrolyte systems are calculated from the intercept of real part of the complex impedance plot, which is bulk resistance of the film, known area and thickness of the film using the equation:

$$\sigma = l/R_b A$$

where l is the thickness of the electrolyte film; R_b the bulk resistance of the electrolyte film; and A is the area of the film.

Conductivity measurement is carried out under vacuum to avoid the film contamination from moisture and by means of ac impedance analysis from electrode effects. The complex impedance diagram describes two well-defined regions: a semicircle in high frequency range which is related to conduction process in the bulk of complex and the linear region in the low frequency range that is attributed to the effect of blocking electrodes. At low frequency, complex impedance plot shows straight line parallel to the imaginary axis, but double layer at blocking electrodes causes the curvature [15]. It is observed that from the impedance plot (Fig. 3), the disappearance of semicircle in high frequency region, which led to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction [16].

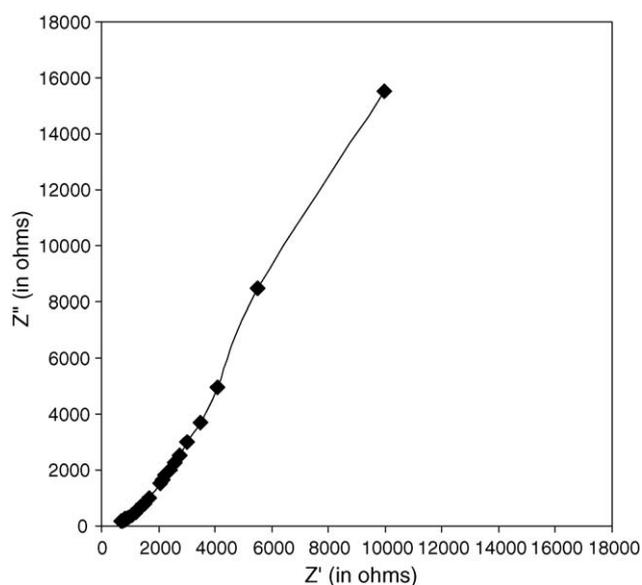


Fig. 3. The complex impedance plot of PVA-PMMA (60:40)- LiBF_4 (10 wt.%) at 302 K.

Table 1 shows the conductivity values of PVA–PMMA–LiBF₄ polymer electrolyte systems. It is observed that PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ complex exhibits maximum conductivity of about $2.8 \times 10^{-5} \text{ S cm}^{-1}$ at ambient temperature. It is also higher than the value (10^{-8} to $10^{-4} \text{ S cm}^{-1}$) reported by Every et al. [8] for PVA–LiCF₃SO₃ system. The conductivity for pure PVA system has been reported as $10^{-10} \text{ S cm}^{-1}$ [17–20].

It is also found that with an increasing PVA content (>60%) in the blend, conductivity gets decreased. A high PVA content imparts high viscosity and makes the mixture more like a rubbery transport solid. Increase in viscosity could be also realized as a macroscopic interactive effect between the polymer and the solution, which affects the mobility. Similar observations are reported by Mishra and Rao for PVA–PEO (60:40) blend [21]. Hence it is found that the optimum blend composition for PVA–PMMA is 60:40 considering both the mechanical stability and ionic conductivity.

According to the free volume theory of polymers, when the temperature is increased the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighbours and create a small amount of space surrounding its own volume in which vibrational motion can occur [22]. The resulting conductivity is represented by overall mobility of ion and polymer, which is determined by the free volume around the polymer chain. Therefore, an increase in temperature produces more free volume, which increases the mobility of ions and segments and hence the conductivity.

The temperature dependence conductivity of the electrolyte films is shown in Fig. 4. No linear dependence could be obtained seems to suggest that ion conduction follows the Williams–Landel–Ferry (WLF) mechanism [23]. In other words, the non-linearity indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion [24]. Thus, the result may be effectively represented by the empirical Vogel–Tamman–Fulcher (VTF) equation

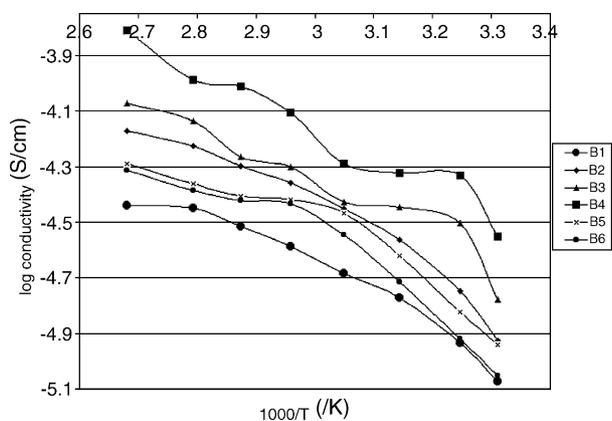


Fig. 4. Arrhenius plot of log conductivity vs. $1000/T$ for $[(1-x)\text{PVA}-x\text{PMMA}]-\text{LiBF}_4$ (10 wt.%) complexes.

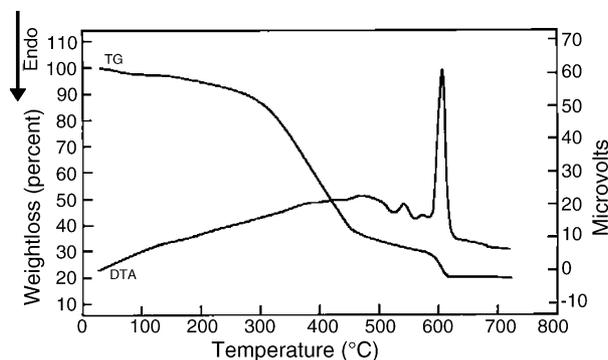


Fig. 5. TG/DTA curve of PVA–PMMA (60:40)–LiBF₄ (10 wt.%) complex.

[24–26]:

$$\sigma = AT^{-1/2} \exp(-B/T - T_0)$$

where A and B are constants and T_0 is the reference temperature. Constant A is related to the number of charge carriers in the electrolyte and B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains. Thus the results for film B1 and B2 may be described by the VTF relation, which describes the transport properties in a viscous matrix and rest of the samples show neither linear, nor VTF behaviour. Thus the non-linearity of the plots suggests that ionic transport in the electrolytes is associated with the polymer segmental motion.

3.4. TG/DTA analysis

TG/DTA analysis is sensitive enough to record the thermal events such as melting, decomposition and corresponding weight loss of the electrolyte sample. The result of thermogravimetric and differential thermal analysis of PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ complex is discussed from TG/DTA curve shown in Fig. 5. It is reported that in pure PVA decomposition occurred in two stages and it was thermally stable up to 265 °C with a weight loss of around 15% [27]. No effort has been made to confirm the decomposition products as it is well known that the decomposition leads to evolution of lower molecular weight alkanes, alkenes, aldehydes, ketones, etc. and also acetaldehyde and acetic acid in case of pure PVA [28–30]. In the case of blend, decomposition occurred in two stages as evidenced from the TG curve of the electrolyte film B4. It is found from the thermogram that there is a residue of about 19% and most of the residue in the electrolyte could be from unhydrolyzed acetate portions of PVA. The blend electrolyte has decomposition temperatures at 295, 458, 594 and 614 °C with corresponding weight losses of about 13, 63, 73 and 81%, respectively. From the TG curve, the film shows a gradual weight loss up to 295 °C. Beyond that temperature, a rapid decrease in weight of the film has been observed. It is inferred from the thermogram that the thermal stability of the film is 295 °C.

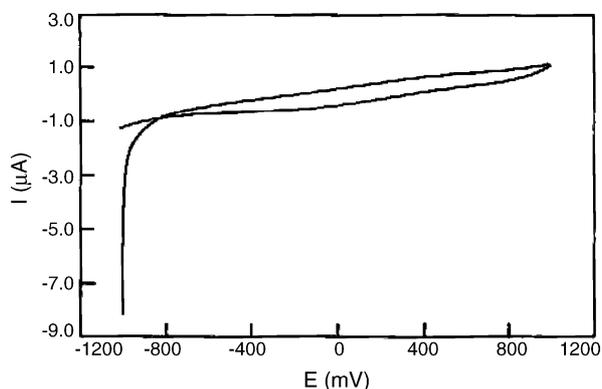


Fig. 6. Cyclic voltammogram of PVA–PMMA (60:40)–LiBF₄ (10 wt.%) complex with SS electrodes; scan rate: 5 mV s⁻¹.

In DTA curve, some exothermic peaks are observed at 498, 541, 593 and 605 °C. A sharp and large exothermic peak at 605 °C concurrent with a significant weight loss of about 80% takes place, indicating the complete decomposition of the film.

3.5. Cyclic voltammetry

Fig. 6 represents the cyclic voltammogram of PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ complex. The cyclic voltammetry has been performed for the SS/polymer electrolyte/SS cell couple with a scan rate of 5 mV s⁻¹ of about 20 cycles to affirm that the electrolytes have an excellent reversibility. CV studies employing SS electrodes have already been carried out by Girish Kumar and Munichandriah [31,32] for the polymer electrolytes based on PVdF and PMMA. The following points are observed from the cyclic voltammogram:

- (i) The electrochemical window has been obtained from –1000 to +1000 mV for PVA–PMMA–LiBF₄ polymer electrolyte.
- (ii) The cathodic and anodic peaks are not observed. This may be due to non-interaction of lithium in the polymer electrolyte with the SS electrodes.

The cyclic voltammogram strongly indicates that the polymer electrolyte has excellent reversibility and cyclability.

4. Conclusions

1. Free-standing, flexible natured polymer electrolytes films based on different compositions of PVA–PMMA–LiBF₄ (10 wt.%) have been prepared. The complexation behaviour of polymer salt matrices has been confirmed from XRD and FTIR studies.
2. The maximum conductivity value has been observed for PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ (10 wt.%) complex. Temperature dependent conductivities of the

samples are discussed on the basis of free volume model.

3. From the TG/DTA curve, thermal stability of PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ (10 wt.%) system is estimated as 295 °C and is preferred in lithium batteries as its operating temperature is normally in the range 40–70 °C [33].
4. Good cyclic and reversible performance has been obtained for the electrolyte PVA (60 wt.%)–PMMA (40 wt.%)–LiBF₄ (10 wt.%).

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