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Compositional effect of PVdF–PEMA blend gel polymer electrolytes for lithium polymer batteries

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Abstract

Owing to their improved mechanical properties and good polymer miscibility, the blend gel polymer electrolytes of poly (vinylidene fluoride) (PVdF)-poly(ethyl methacrylate) (PEMA) have been prepared using solvent casting technique and characterized for their electrochemical performances. The electrolyte shows a maximum ionic conductivity of 1.5×10^{-4} S cm^{-1} at 301 K for the 90:10 blend ratio of PVdF:PEMA system with good transport property. The ionic conductivity is enhanced, in accompany with improved microstructural homogeneity, at low PEMA contents, while the decreased conductivity at high contents has been attributed to increasing crystalline PEMA domains. With the optimum PVdF:PEMA ratio, the complex system was found to facile reasonable ionic transference number and exhibit superior interfacial stability with Li electrode.
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1. Introduction

Since the first report of high conductivity in gel polymer electrolytes (GPEs), these materials, which have both solid and liquid like properties, was introduced as a novel material in the field of lithium rechargeable battery applications [1,2]. In GPEs, the polymers are swelled in solvents containing ions. Simply, this can be thought as a non-aqueous liquid electrolyte immobilized by a polymer matrix.

The salt retained within the matrix provides ions for conduction and the solvent helps in the dissolution of the salt and also provides the medium for ion conduction. GPEs comprise polymers such as poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(acrylonitrile) (PAN), poly(vinyl pyrrolidone) (PVP) and poly(vinyl sulfone) (PVS) [2–4]. These electrolytes were found to possess ionic conductivity, electrochemical stability and transport properties (similar to their liquid counter parts) with dynamical properties, suitable for rechargeable Li-ion battery applications. Hence GPEs are also the preferred choice for new generation Li-ion batteries.

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PVdF has been a favourable choice as polymer electrolyte. Recently PVdF based GPEs have demonstrated sufficient conductivity (10^{-5}–10^{-3} S cm^{-1}) for commercial usage in secondary batteries [5]. On the other hand, the methacrylic ester polymers have excellent chemical resistance, high surface resistivity, and mechanical properties, etc. The most common polymer in this group is poly(methyl methacrylate) (PMMA), and because of its high resistance, non-tacking characteristics, surface resistance, optical properties, etc., it has been intensively investigated by several researchers [6–8]. Han et al. [9] reported that the mechanical strength of PVC/poly(ethyl methacrylate) (PEMA) based electrolytes was found to be much higher than that of PVC/PMMA based electrolytes. Indeed, the elongation strength of PEMA (7%) is higher and its T_g (336 K) [10] is lower as compared to PMMA. The negative interaction parameter of PVdF–PEMA blend [11] suggests good mutual compatibility. Proof of the blend concept was demonstrated with PVdF/PEMA polymer electrolyte by Kwei et al. [12] Our preliminary tests indicated that the PVdF/PEMA based GPEs also exhibit greater mechanical strengths than their PMMA counterparts. For instance, the GPE made from the blend of PVdF(27)–PEMA(3)–LiClO$_4$(5)–Ethylene carbonate (EC) (32.5):Propylene carbonate (PC) (32.5) wt% exhibited a storage modulus of ~390 MPa, which is nearly 17 times that of its PMMA counterpart at room temperature (298 K). To our knowledge, there has not been literature in characterizing the electrochemical properties of this particular GPE system. In this work, studies have been carried out to investigate the composition effect of PEMA in PVdF based electrolytes in the view point of ionic conductivity and electrochemical properties. The electrolytes comprising PVdF, PEMA, LiClO$_4$, EC and PC have been prepared using solution casting technique. The prepared electrolytes were characterized for its ionic conductivity, electrochemical stability windows, lithium ion transference number and compatibility with the lithium metal electrode, etc., and the results are discussed on conductivity basis.

2. Experimental

The matrix polymers for the gel polymer electrolytes namely, PEMA with average molecular weight of 515,000 and PVdF with average molecular weight of 534,000 were purchased from Sigma–Aldrich and Aldrich, USA respectively. LiClO$_4$ was used as the electrolyte salt, since it shows smaller dissociation energy [13]. As plasticizers, EC (Aldrich, USA) and PC (Fluka) were used without further purification. All the polymers, salt and plasticizers were dissolved in an anhydrous tetrahydrofuran (THF) purchased from Fluka.

Table 1 summarizes the compositions (SA1 to SA6) of the electrolytes and hereafter can be discussed with their sample codes. Preparation of the GPEs involves the admixture of a plasticizing solvent and a salt into a polymer matrix. The mixture is continuously stirred for about 24 h at ambient temperature, so that uniform gel is formed. Films were prepared by using the solvent casting technique [14] and further traces of the solvent were removed by drying the films at 323 K (50 °C) for 24 h in the temperature controlled vacuum oven. All the preparation, stirring, casting and cell assembling for characterization were carried out in a dry room having a dew point between 228 and 233 K (−45 and −40 °C).

The impedance studies were carried out by sandwiching the electrolytes between stainless steel (SS) electrodes, and the impedance was measured with the signal amplitude of 10 mV in the temperature range 301–373 K. The electrochemical studies of the electrolytes were performed using ECO CHEMIE PGSTAT 30. The interfacial resistance was also measured using the same impedance technique

Table 1
Ionic conductivity values at 301 K, activation energy and lithium ion transference number values of PVdF:PEMA(50 wt%)–LiClO$_4$(5 wt%)–EC + PC(1:1 ratio) (45 wt%) electrolytes

Sample	Compositions of PVdF:PEMA–LiClO$_4$–EC + PC (g)	σ at 301 K ($\times 10^{-4}$ S cm^{-1})	E_a (eV)	t_+
SA1	0.50:0.0 − 0.05 − 0.225 + 0.225	0.20	0.43	0.7
SA2	0.45:0.05 − 0.05 − 0.225 + 0.225	1.47	0.3	0.67
SA3	0.40:0.10 − 0.05 − 0.225 + 0.225	0.94	0.32	0.60
SA4	0.35:0.15 − 0.05 − 0.225 + 0.225	0.26	0.35	0.62
SA5	0.30:0.20 − 0.05 − 0.225 + 0.225	0.015	0.41	0.58
SA6	0.25:0.25 − 0.05 − 0.225 + 0.225	0.0028	0.46	0.49

for lithium symmetric cell. The electrochemical stability of the electrolytes was determined using the linear sweep voltammetry (LSV) for SS/GPE/Li cell assemble at 1 mV/sec from its OCP to 6 V. The lithium symmetric cell couple was used for lithium ion transference number measurement by polarization technique for constant dc voltage of 5 mV. The surface morphology of the prepared electrolytes was examined by JEOL JSM-5310 scanning electron microscope (SEM). The samples were sputtered with Pt coating and then examined under vacuum. The X-ray diffraction analysis (XRD) of the electrolytes was carried out by Philips' X'pert X-ray diffractometer.

3. Results and discussion

3.1. Microstructures and conductivity

XRD analysis of the pure PVdF GPE (Fig. 1 SA1) showed characteristic diffraction peaks, respectively at $2\theta = 18.7°$ and $20.8°$, of pure PVdF [15]. The crystalline domain size is estimated to be $\sim$3 nm, as calculated from Scherrer's equation. None of the diffraction peak pertaining to $LiClO_4$ is observed, indicating that the electrolyte salt is completely dissolved. The pattern remains essentially unchanged with addition of PEMA up to the SA2 composition. However, with further increasing PEMA content, additional diffraction peaks, suggesting formation of a new crystalline phase, emerged near $2\theta = 12°$ and $27°$ (Fig. 2 SA6). The broad nature of these new peaks suggests rather small domain sizes.
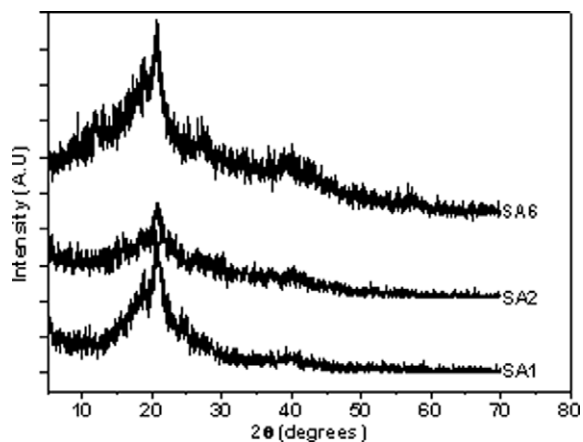
SEM analysis shows that the pure PVdF GPE has a granular microstructure (Fig. 2a). The granules have sizes between 5 and 6 μm, suggesting that every granule is an assembly of many crystalline domains. After adding PEMA, the interaction between PVdF and PEMA is appreciable. The interaction produces a more relaxed network in the matrix, and the structure becomes increasingly homogeneous (Fig. 2b–f). The average granule size appeared to be monotonically and markedly decreases with increasing PEMA content.

The Nyquist impedance plots of all the samples in general consist of a high-frequency semicircle and an inclined line toward low frequencies. The intercept of the semicircle with the real axis gives bulk resistance [16]. The semicircle, on the other hand, arises from coupled resistance/capacitance (R/C) at the electrolyte/electrode interface. As shown in Fig. 3a with increasing PEMA content, the complex plot was found to first shift to the left, i.e., to lower resistances, and then to the right with the minimum bulk resistance taking place at the composition of PVDF:PEMA = 90:10 (sample SA2). In addition, at high PEMA contents (SA5, SA6), the radius of the semicircle, and hence the interfacial resistance was found to dramatically increase with increasing PEMA content.

From Table 1 it is inferred that the maximum ionic conductivity value has been observed for the sample SA2 of 1.47×10^{-4} S cm^{-1} at 301 K. It is higher than the value $\sim 10^{-6}$ S cm^{-1} at room temperature for PVdF–HFP/LiClO$_4$/EC+PC based electrolytes reported by Stephan et al. [17]. It is comparable with the value 1.8×10^{-4} S cm^{-1} reported by Shen et al. [18] for PVdF/LiClO$_4$ (5 wt%) wetted by EC/PC mixture of 0.1 M LiClO$_4$ polymer electrolyte system. The ionic conductivity of SA2 is enhanced by one order of magnitude when comparing the sample containing PVDF only. However, further addition of PEMA content decreases the conductivity value up to three orders of magnitude from the maximum.

It is well known that the ionic conductivities of gel polymer electrolytes strongly depend on temperature. The complex impedance plot of SA2 is shown in Fig. 3b within the temperature range of 301–373 K. Ionic conductivities of these films derived from the impedance spectroscopy revealed an increase with temperature. Arrhenius plots, which correlate conductivity (σ) with temperature (T) in the form of

$$\sigma = \sigma_0 \exp(-E_a/RT)$$

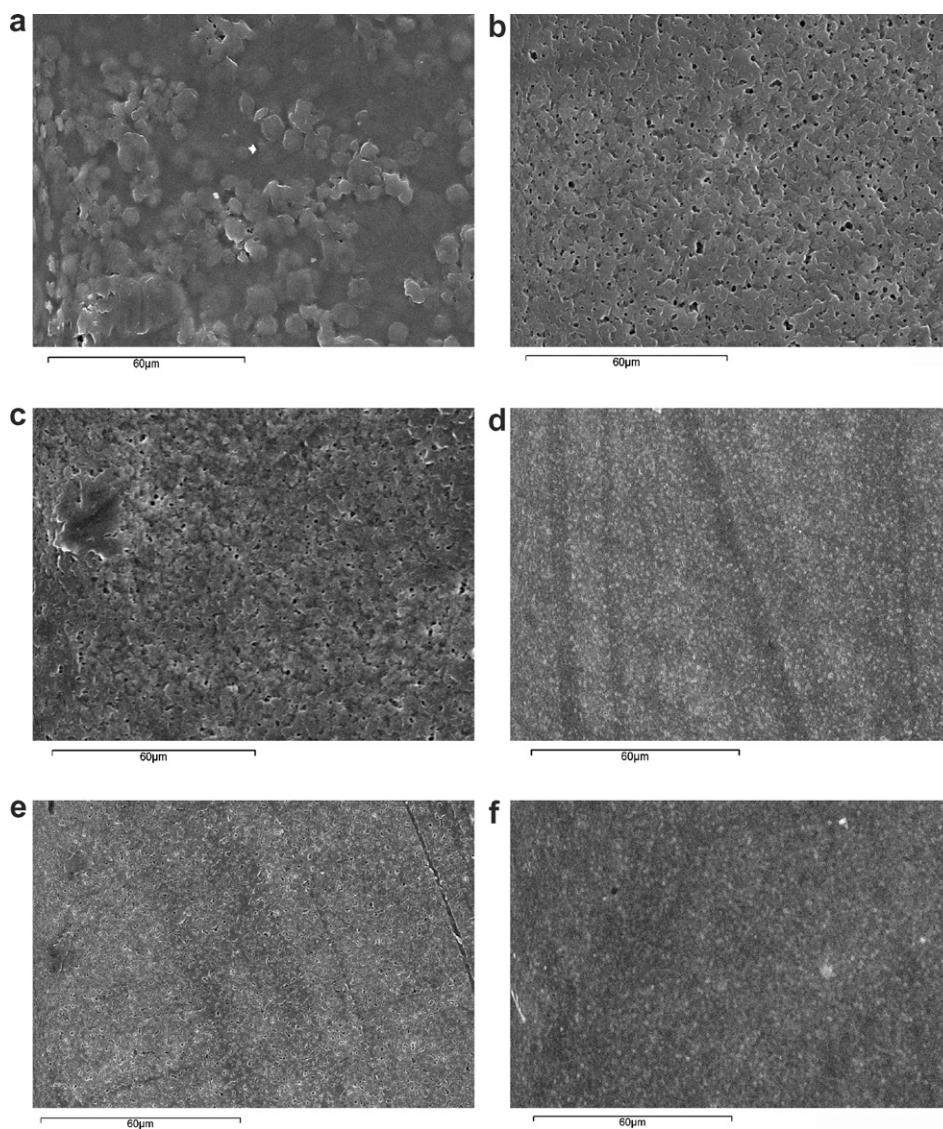Fig. 1. XRD spectra of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% electrolytes.

Fig. 2. SEM images of (a) 100:0, (b) 90:10, (c) 80:20, (d) 70:30, (e) 60:40 and (f) 50:50 compositions of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% based electrolytes.

of the GPEs within the temperature range 301–373 K are shown in Fig. 4. The correlated E_a values are listed in Table 1. The activation energy varies within the range of 0.3–0.46 eV (29–44 kJ/mol) with the minimum activation energy occurring at the same composition (SA2) that gives the highest conductivity. One notes that these activation energies are significantly larger than that 0.15 eV (14.5 kJ/mol) typical for Li salt solutions with organic solvents. This may indicate strong interaction between the electrolyte ions and the polymer matrix within the present GPEs.

The initial increase in ionic conductivity with PEMA addition may be caused by the degree of interaction between matrix polymer and aprotic solvent. Since the ethyl methacrylate unit has carbonyl group in the side chain, it can be presumed that EMA unit is more compatible with carbonate groups compared to other groups. Thus it is believed that the addition of PEMA causes the interaction between its carbonyl group with fluorine in PVdF and with carbonate groups of the plasticizers. This enhances the overall compatibility between the polymer matrix and the plasticizers, and it is
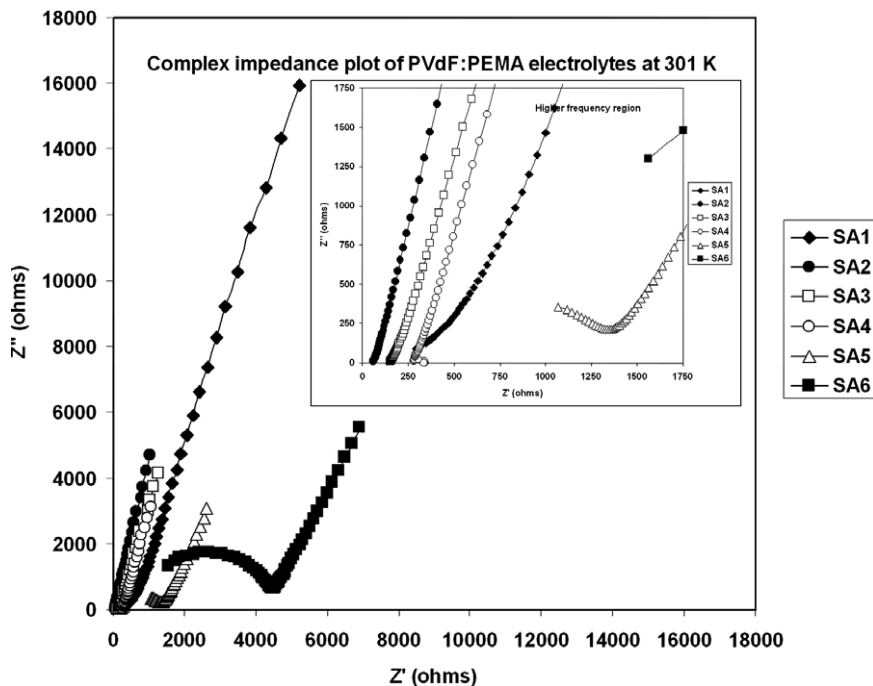
Fig. 3a. Complex impedance plot of 90:10 ratio PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% based electrolyte in the temperature range 301–373 K.
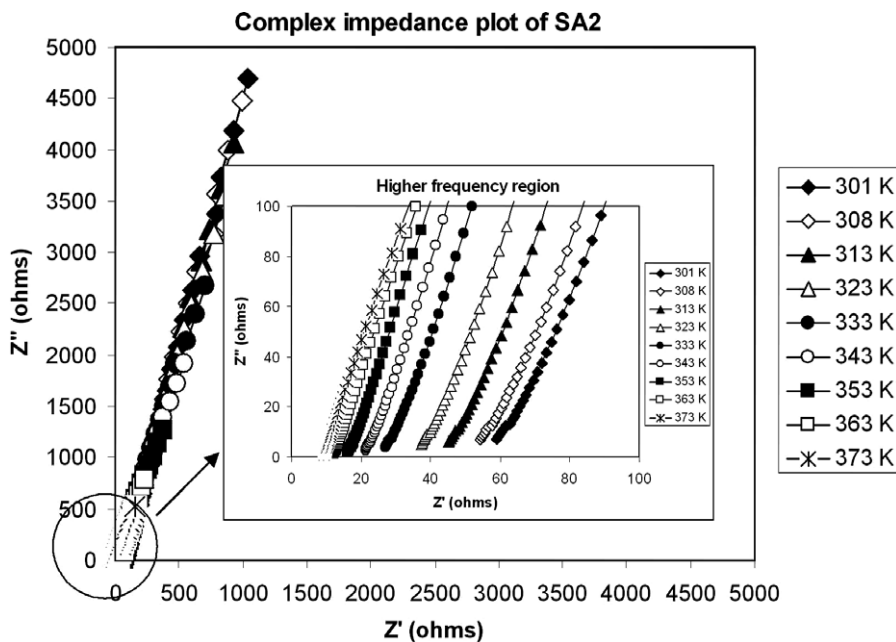

Fig. 3b. Complex impedance plots of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC+PC(45) wt% electrolytes at 301 K.

reflected by the decreased granule size in the GPE microstructure, as revealed by SEM (Fig. 2a–f). As the plasticizers penetrate to fill homogeneously in between PVdF crystalline domains, electrolyte ions diffuse through a more liquid-like medium in contrast with the "dry" PVdF domains. This results
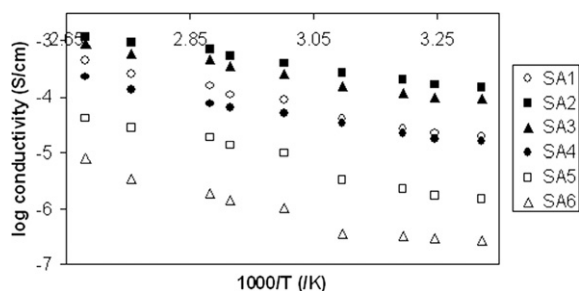
Fig. 4. Temperature dependent ionic conductivity plots of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% based electrolytes in the temperature range 301–373 K.

in a higher conductivity as well as lower activation energy. However, aggregation of the ester group of PEMA forming new crystalline domains could occur with increasing PEMA content. The domains may cover some polar domains of PVdF and hence reduces the interaction between the electrolyte ions and polar section of the polymer matrix. This may explain the reduction in ionic conductivity as PEMA content increases to pass an optimum concentration. Furthermore, as ion conduction of Li

salts in poly methacrylate matrix typically exhibited higher activation energy than in PVdF [19], the increased PEMA domain is expected to lead to an increase in average activation energy.

3.2. Electrochemical stability determination

The electrochemical stability window of the electrolytes is analyzed using the linear sweep voltammetry (LSV) and the voltammograms as shown in Fig. 5. It is evident that from the current response curve, there is no obvious current through the working electrode from open circuit potential to 4.5 V versus Li$^+$/Li and then the current related to the decomposition of the electrolyte is gradually increased beyond 4.5 V for all the samples. The decomposition current above 4.5 V was found to decrease monotonically with increasing PEMA content up to the SA5 composition (PVdF:PEMA = 60:40). It increases again when PEMA content increases further. It is evident that the electrolytes SA2 and SA3 have favourable electrochemical stability and also higher ionic conductivity than pure
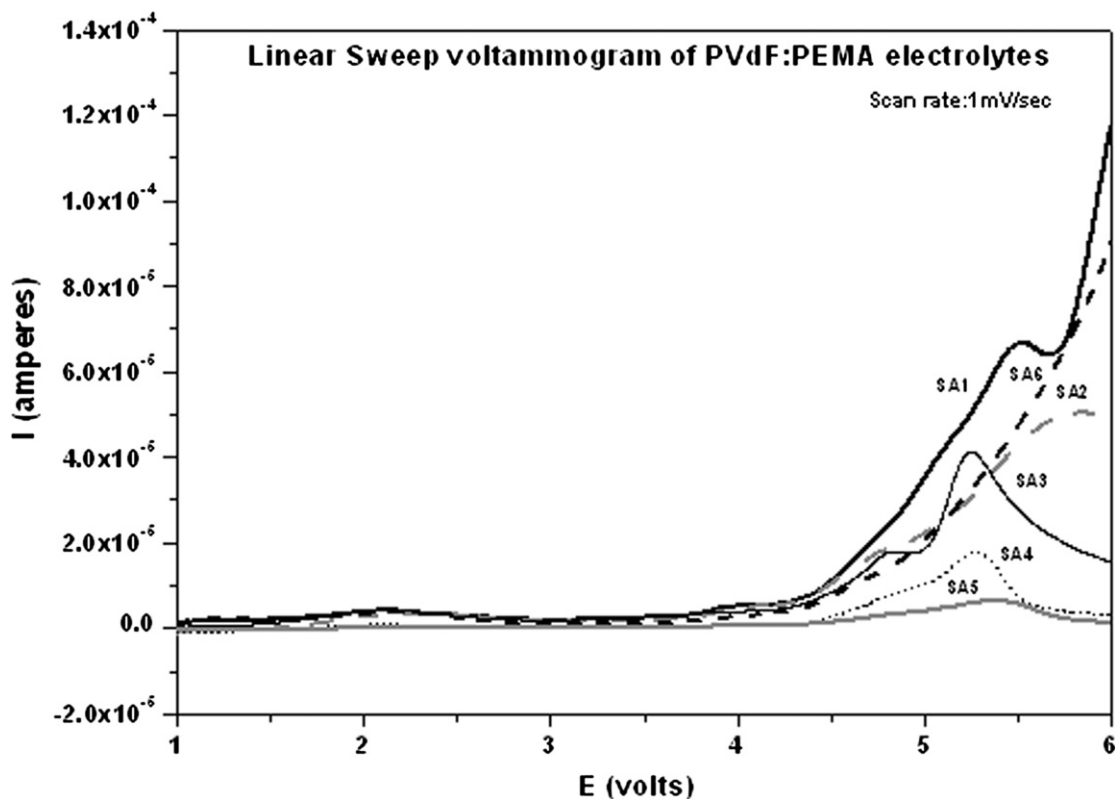

Fig. 5. Linear sweep voltammograms of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% based electrolytes at the scan rate 1 mV/s.
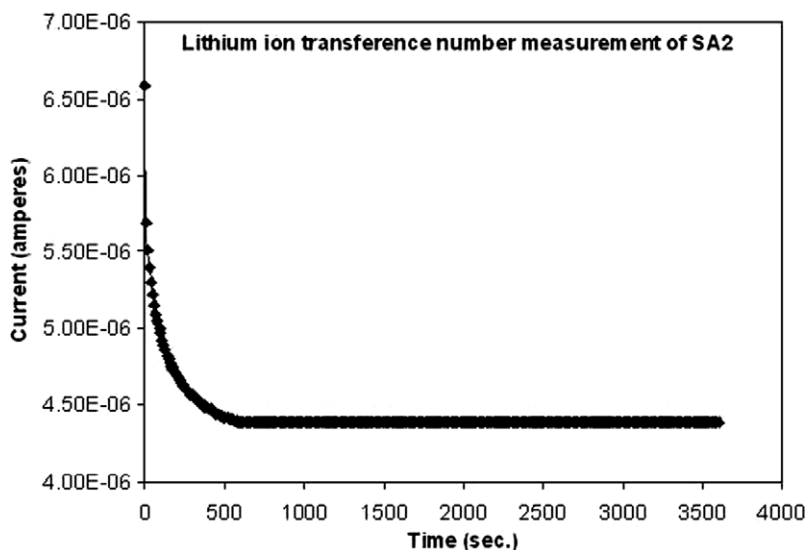
Fig. 6. Polarization current versus time curve of 90:10 ratio of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% electrolyte.

PVdF, and it reveals that these electrolyte compositions would be suitable for Li battery applications.

3.3. Ionic transference number measurements

Another important parameter in the electrolyte's performance is the ionic transference number; usually polymer electrolytes have the values less than unity. The current versus time graph of sample SA2 is shown in Fig. 6. The transference number measurements were carried out for all samples and the values are listed in the Table 1. The electrolyte exhibiting maximum conductivity has ionic transference number of 0.67 and it is more suitable for the lithium battery fabrication. It is in well agreement with the theory [20].

3.4. Interfacial resistance measurements

In the polymer electrolyte systems, a resistive layer covers the lithium and the resistance of this layer grows with time, and the structure of this layer is not understood. It is known that the uncontrolled passivation phenomena can play a vital role in cyclability, shelf life, dissolution efficiency, etc. of the battery [21]. In the present study, the interfacial resistance evaluation was performed on symmetric lithium cells with the prepared electrolytes at ambient temperature. The impedance of the cell was monitored with time by using the impedance analysis for the samples SA2 and SA3 (see Fig. 7). It
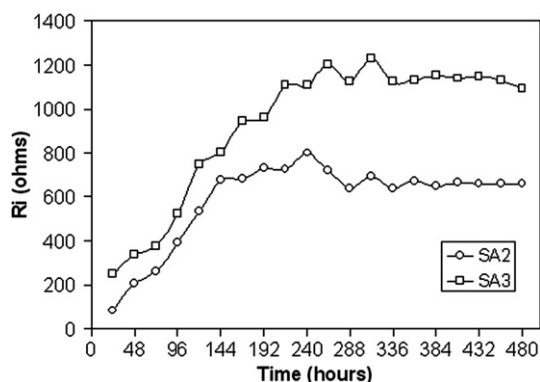

Fig. 7. Time evolution of interfacial resistance Ri of lithium electrode at ambient temperature with 90:10 and 80:20 ratio of PVdF:PEMA(50)–LiClO$_4$(5)–(1:1) of EC + PC(45) wt% electrolytes.

is obvious that the possible reasons for the formation of passivation layer are the ester group of PEMA and plasticizers' effect in the electrolyte. It was found that the values of interfacial resistance, Ri, are minimum for SA2. The increment of Ri values for SA3 may be due to more protective ester layer was formed on the lithium surface. On the other hand, the propylene carbonate that acts as a plasticizer may decompose in the presence of lithium and form propylene and Li$_2$CO$_3$. Poly propylene oxide and carbon dioxide may be formed as a result of polymerization of propylene carbonate. This results in the formation of some polymer cross-links through free radical couplings in the

presence of lithium metal and hence the passivation layer [22].

4. Conclusions

The plasticized PVdF/PEMA polymer electrolytes have been prepared for various compositions, by solvent casting technique. The optimum blend composition has been observed for the electrolyte with 90:10 ratio of PVdF:PEMA in terms of ionic conductivity and interfacial property. The ionic conductivity is enhanced while adding PEMA with PVdF, presumably due to increased compatibility between the polymer and plasticizers. On the other hand, the conductivity subsequently decreases with increasing PEMA domains at high contents. The temperature dependence of conductivity also indicated minimum activation energy associated with the maximum conductivity composition. With the optimum PVdF:PEMA ratio, the GPE system was found to facile reasonable ionic transference number and exhibit improved interfacial stability with Li electrode.

Acknowledgments

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