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Effect of various plasticizers on the ionic conductivity of PVAc/ PEMA based polymer blend electrolytes for lithium rechargeable batteries

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Abstract — *Poly (ethyl methacrylate) (PEMA) and Poly (vinyl acetate) (PVAc) blended solvent free gel polymer electrolytes were prepared with* $LiClO_4$ *salt and various plasticizers (Ethylene Carbonate (EC), Propylene Carbonate (PC) and γ-Butyrolactone (GBL)) by solvent casting technique. The structural reorganization of the prepared samples has been confirmed from XRD analysis Comparison of the ionic conductivity values of the electrolyte membranes with different plasticizers is done using ac impedance analysis and the maximum ionic conductivity of* 8.073×10^{-4} Scm^{-1} *at room temperature has been obtained for the sample with EC as plasticizer. The Vogel-Tamman-Fulcher (VTF) relation holds good for this system due to the non-linear variation of conductivity with temperature. The porous nature of the gel polymer electrolytes is identified from the scanning electron microscopic (SEM) images.*

Keywords*- Different plasticizers, structural reorganization, Ionic conductivity, VTF relation, Porosity.*

I. INTRODUCTION

For few decades, an immense research on polymer electrolytes has been carried out due to their potential applications in the fields of electrochromic devices, rechargeable lithium ion batteries, hybrid electric vehicles, etc. [1,2]. The polymer electrolytes with high ionic conductivity and excellent mechanical properties at room temperature remains a challenge in the fabrication of safe, reliable and high energy density lithium batteries. To improve the various physical properties of the polymer electrolytes,the Gel Polymer Electrolytes (GPE) are prepared. The GPEs are prepared by the incorporation of low molecular weight plasticizers into the polymer matrix. The Crystallinity and segmental motion being identified as the main parameters in controlling the ionic conductivity, it becomes essential to use additives, known as plasticizers which act as interchain lubricants. Plasticizers are organic solvents having low glass transition temperature (T_g) and high dielectric constant, aids in the mobility of ions and hence leads to high ionic conductivity. The high dielectric constant of the plasticizers increases the dissociation of salt, thereby enhancing the free charge carriers in the electrolyte material. The gel polymer electrolytes also known as hybrid polymer electrolytes exhibit features such as high lithium ion mobility, flexible structure, low glass transition temperature and high thermal stability. The GPEs are preferred as they possess the combined properties of liquid and solid electrolytes such as diffusion and cohesion respectively. The enhancement in ionic conductivity is achieved by the use of plasticizers such as Propylene Carbonate (PC) [3], Ethylene Carbonate (PC) [4], γ-Butyrolactone (GBL) [5]. The desired parameters such as polymer-ion interaction, reduction in T_g values, lowering the viscosity, increasing the dissociation of salt to make the polymer electrolyte a best choice for rechargeable lithium batteries are made possible by the plasticizing effect.

In the present work, an attempt has been made to investigate the effect of various plasticizers such as EC, PC and GBL in tuning the ionic conductivity of PEMA/PVAc based polymer blend electrolytes with $LiClO_4$ salt as the donor of charge carriers. Several works on GPEs reveal that all the plasticized polymer electrolytes lose their mechanical strength upon the addition of plasticizers and leads to poor interfacial properties [6-8]. To improve the mechanical strength of the polymer electrolytes, Poly(ethyl methacrylate) (PEMA) has been used as a host polymer in this work. The works on PEMA based polymer electrolytes reveal that the polymer PEMA acts as a mechanical stiffener [9-11]. In this work, PEMA has been blended with the polymer Poly(vinyl acetate) (PVAc), since PVAc also helps in improving the mechanical property of the electrolyte [12]. The $LiClO_4$ salt has been used in the present study due to its low dissociation energy and higher anionic radius. The prepared Gel polymer electrolytes PEMA/PVAc (70/30 wt%)/$LiClO_4$ (8 wt%) with various plasticizers are subjected to various experimental investigations.

II. EXPERIMENTAL TECHNIQUES

PEMA (M_w ~ 515,000), PVAc (140,000) and $LiClO_4$ were purchased from Aldrich chemicals limited, USA and dried under vacuum at 100°C for 24 hours before use. The plasticizers ethylene carbonate (EC, USA), propylene carbonate (PC, Merk-Germany) and γ-butyrolactone (GBL, Alfa Aesar-India) and the solvent tetrahydrofuran (THF) were used as received. An appropriate amount of PEMA/PVAc (70/30 wt%), $LiClO_4$ (8 wt%) and 69 wt% of EC, PC and GBL were dissolved in anhydrous THF separately. Then these solutions were mixed together and stirred continuously for 24 hours with the help of a magnetic stirrer until a homogeneous mixture was obtained. Then the resultant solution was poured in the petri dish and the solvent THF was allowed to evaporate slowly at 40°C in the vacuum oven under 10^{-3} Torr pressure for 24h. The PEMA/PVAc/$LiClO_4$/X (where X=EC, PC, GBL) based gel polymer electrolyte films so obtained were further heated at 60°C to remove the trace of solvent, if any. The films were examined for its dryness and free standing nature. The prepared gel polymer electrolyte membranes were then subjected to various characterization techniques. The structural analysis was carried out by X-ray diffractometer (X'pert PRO PANalytical). The ac impedance study was carried out on the polymer electrolyte films using a computer controlled micro autolab Type III Potentiostat/Galvanostat in the frequency range of 40 Hz – 300 KHz. Scanning electron microscope (JEOL, IXA-840 Japan) was employed for morphological studies.

III. RESULTS AND DISCUSSIONS

A. XRD Analysis

The intensity of X-ray diffraction peaks and the changes undergone in the X-ray diffractogram due to the incorporation of new components in the polymer matrix provide reliable and precise information on the nature of the sample, phase-structure and microstructural aspect of a system. Figure. 1 (a) depicts the XRD patterns of pure $LiClO_4$, PEMA, PVAc and polymer gel complexes. The XRD spectrum of pure $LiClO_4$ exhibits sharp, intense peaks at the diffraction angle of 2θ = 20.9, 23, 27, 32.99 and 35.4°, illustrating the high crystalline nature of the $LiClO_4$ salt. The X-ray diffractogram of PEMA shows peaks at 2θ = 13 and 18°. The two broad peaks observed at 2θ = 14.5 and 22° in the diffractogram of PVAc reveal the amorphous nature of the polymer. The diffractograms Figure. 1(b) of PEMA/PVAc/$LiClO_4$ polymer blend electrolytes with various plasticizers do not show significant peaks pertaining to $LiClO_4$ indicating the complete dissolution of the salt. The reduction in the intensity of the diffraction peaks of the polymer complexes clearly picturizes the occurrence of phase transition where the samples have switched to the rich amorphous phase. The preferred amorphous phase of the polymer electrolytes favors the segmental mobility of the polymer matrix, leading to an enhanced ionic mobility [13]. The observed reduction in the crystallinity of the polymer electrolyte films is the result of the interaction between the polymer and plasticizers, which brings about a structural reorganization in the electrolyte system [14].

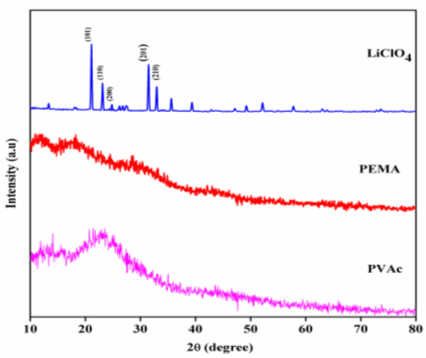


Figure 1 (a). XRD patterns of pure $LiClO_4$, PVAc, PEMA

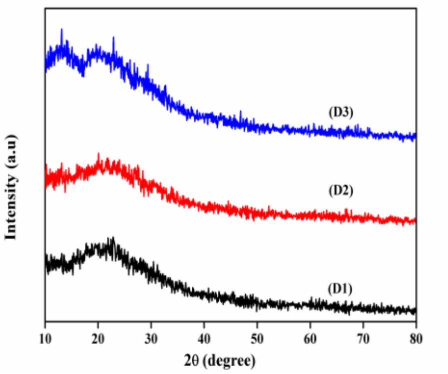


Figure 1 (b). XRD patterns of the prepared complexes

B. Conductivity analysis

Impedance spectroscopic analysis

The typical impedance plots of PEMA/PVAc (70/30 wt%)/$LiClO_4$ (8wt%)/plasticizer (x) (69 wt%) (where x = EC, PC,GBL) gel polymer electrolytes at room temperature are depicted in Fig. 2(a). The complex impedance plots displayed two well defined regions, the high frequency semi-circular portion followed by a low frequency spike. The semi-circular portion is due to the bulk response of the electrolyte whereas the low frequency spike is the outcome of a blocking double layer capacitance effect. The intercept of the low frequency spike on the Z' axis gives the bulk resistance value. The ionic conductivity of the electrolyte is calculated using the formula,

$$\sigma=L/(R_bA)$$

The dielectric constant and viscosity values of the plasticizers used in the polymer electrolytes are listed in Table 1. The ionic conductivity values of the prepared samples at various temperatures (303 K – 363 K) are summarized in Table 2.

The ionic conductivity values are found to vary from 6.295×10^{-4} Scm^{-1} to 8.073×10^{-4} Scm^{-1} at room temperature. The maximum room temperature ionic conductivity of 8.073×10^{-4} Scm^{-1} is obtained for the gel polymer electrolyte with EC as plasticizer. This may be attributed to the high dielectric constant of EC. The high dielectric constant of organic solvents allowed a greater dissociation of the lithium salt and increases the mobility of cation [15]. The ionic mobility and number of carrier ions are the two important parameters responsible for the improved conductivity in polymer electrolytes [16]. The high dielectric constant and low viscosity value of EC enhances the dissociation of $LiClO_4$salt and ionic mobility respectively. Thus the overall ionic conductivity is determined by the dissociation of salt, and the ionic mobility is governed by the viscosity, plasticizer's dielectric constant and the polymer used [17].

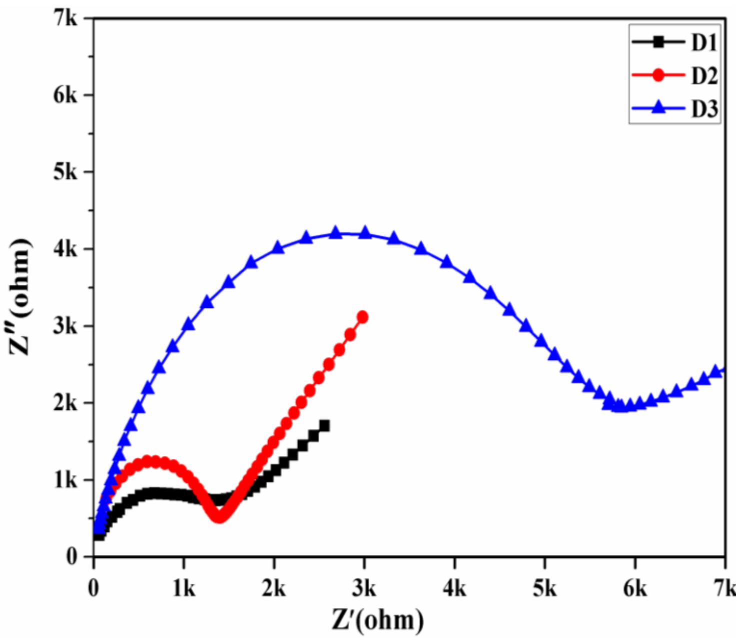


Figure 2 (a). Complex impedance plot of all samples at 303K

Table 1.The dielectric constant and viscosity values of the plasticizers

PLASTICIZER	DIELECTRIC CONSTANT	VISCOSITY (Cp)
Ethylene Carbonate (EC)	89.6	1.86
Propylene Carbonate (PC)	64.4	2.53
γ –butyrolactone (GBL)	39.1	1.75

Table 2.Temperature dependent conductivity values of the prepared samples

SAMPLE CODE	**COMPOSITIONS OF PREPARED SAMPLES (wt%) 70-30-8-69**	**IONIC CONDUCTIVITY X 10^{-4} Scm^{-1}**						
		303K	**313K**	**323K**	**333K**	**343K**	**353K**	**363K**
D1	PEMA-PVAc-$LiClO_4$-EC	8.073	8.149	8.572	8.804	8.976	9.126	9.357
D2	PEMA-PVAc-$LiClO_4$-PC	7.513	7.692	7.819	8.024	8.136	8.377	8.512
D3	PEMA-PVAc-$LiClO_4$-γBL	6.295	6.406	6.543	6.686	6.821	7.015	7.224

Temperature dependence conductivity

The ac impedance plots of gel polymer electrolyte exhibiting maximum ionic conductivity at various temperatures of 303 K-363 K are illustrated in Fig. 2(b). As temperature increases, it has been observed that the bulk resistance of the electrolyte decreases and hence the ionic conductivity increases. The minimum conductivity of 8.073×10^{-4} Scm^{-1} at 303 K temperature and a maximum value of 10.357×10^{-4} Scm^{-1} at 363 K has been obtained for the gel polymer electrolyte with EC as plasticizer. The temperature dependent behavior of ionic conductivity can be understood in terms of free volume model [18]. The thermal expansion of polymer produces free volume into which the ions and the polymer segments can move freely without any hindrance. The availability of free volume decides the ionic mobility and hence the ionic conductivity of the polymer electrolyte system. Thus the increase in free volume with temperature leads to an increase in ionic conductivity. The variation of log conductivity with the inverse absolute temperature is shown in Fig.2 (c). The non-linear behavior of ionic conductivity seems to obey the Vogel-Tamman-Fulcher (VTF) relation[19-21],

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

where A and B are constants, T is the temperature of the sample and T_0 is the temperature at which the configuration entropy becomes zero. The VTF relation helps to correlate the transport properties to the viscoelastic nature of the polymer electrolytes [22]. The incorporation of EC into the PEMA/PVAc/$LiClO_4$ polymer electrolyte aids the mobility of Li^+ ions in the polymer matrix by reducing the viscosity of the complex.

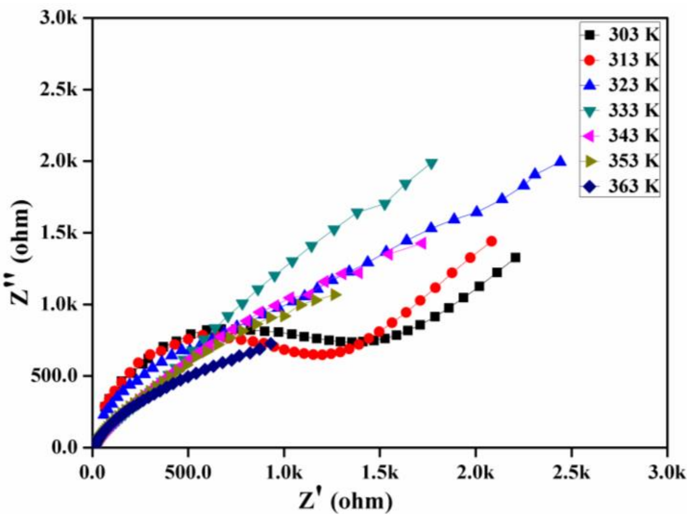


Figure 2 (b). Complex impedance plot of maximum ionic conductivity sample at different temperatures

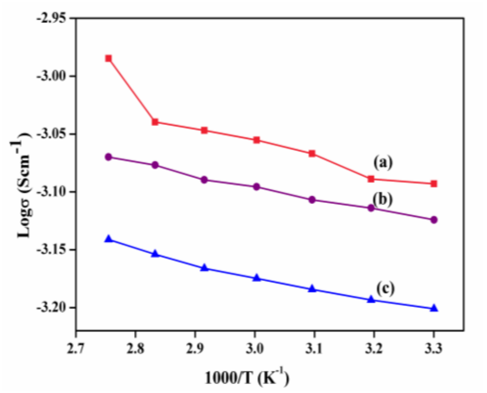
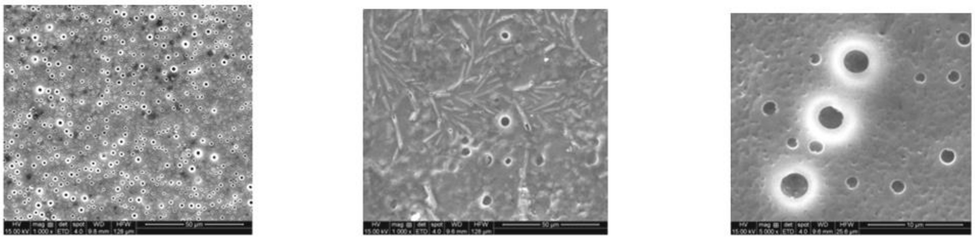


Figure 2 (c). Arrhenius plot of PEMA/PVAc/LiClO$_4$/X gel polymer blend electrolytes where X= (a) EC (b) PC (c) GBL

C. SEM analysis

The SEM micrographs of the prepared samples are presented in Fig. 3. The appearance of pores in SEM images is due to the rapid evaporation of the solvent THF. The pore size is not identical in the SEM photographs of the prepared gel polymer electrolytes. The two important processes, namely, the interaction of the solvent with the polymers and the rate of evaporation of the solvent are responsible in determining the pore formation [23]. The maximum number of pores is observed in the SEM image of the sample containing the plasticizer EC. The maximum porosity leads to the large intake of the electrolyte solution and hence results in maximum ionic conductivity [24]. Thus the gel polymer electrolyte with EC having maximum number of pores has large electrolyte retaining capacity, improves the ion transport mechanism and hence the ionic conductivity. This is in line with the conductivity results obtained from ac impedance spectroscopy.



D1 **D2** **D3**

Figure 3. SEM images of the prepared polymer gel complexes

IV. CONCLUSIONS

PEMA/PVAc /LiClO$_4$/X (where X = EC, PC and GBL) blend gel polymer electrolytes have been prepared by solution-casting technique. The XRD spectra of the prepared samples confirm the structural reorganization in the prepared samples. The ac impedance technique carried out in the temperature range of 303 K-363 K provides information about the ionic conductivity of the prepared samples. The maximum room temperature conductivity of 8.073×10^{-4} Scm^{-1} has been obtained for the blend gel polymer electrolyte with EC added as plasticizer. The high ionic conductivity yielded for EC incorporated blend gel polymer electrolyte is due to the high dielectric constant of EC in comparison to the dielectric constants of PC and GBL, leading to high dissociation of the salt. The ionic conductivity shows a non-linear variation with temperature indicating that the temperature is an important parameter that affects the free volume of the sample and hence the ionic conductivity. The SEM images reveal the high porous nature of the electrolyte with EC. These pores provide a connecting pathway for the ionic motion. Thus the gel polymer electrolyte PEMA/PVAc/LiClO$_4$/EC with maximum conductivity may be a promising candidate for secondary lithium rechargeable batteries.

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