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SHORT COMMUNICATION

Analysis of plasticizer influence in Poly(vinyl acetate)/Poly (vinylidene fluoride) polymer blend electrolyte

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Abstract Gel polymer electrolyte based on poly(vinyl acetate) and poly(vinylidene fluoride) was prepared by solvent casting technique, in which the addition of plasticizers improves the conductivity of polymer membranes. The blend polymer electrolyte containing propylene carbonate (PC) exhibits the highest conductivity of 0.922×10^{-2} S cm^{-1} at room temperature because of the higher dielectric constant as compared to other plasticizers used in the present study. Material characterizations were done with the help of SEM and FT-IR techniques. The activation energy values were computed from 'log σ−1/T' Arrhenius plots.

Keywords Polymer electrolytes · Ionic conductivity · Electrochemical characterizations

Introduction

Polymer electrolytes have been extensively studied in recent years due to their applications in various electrochemical devices, such as high-energy-density batteries, electrochromic devices, and chemical sensors [1–3]. The good mechanical stability and easy film-forming properties of Poly(vinyl acetate) gave an interest on PVAc-based electrolyte systems. Animitsan et al. [4] reported that PVAc-based lithium electrolytes have conductivity in the range from 10^{-5} to 10^{-3} S cm^{-1}. The most straightforward approach to overcome the amorphous nature of PVAc systems is to modify the solvating polymer in order to reduce the amorphicity and glass transition temperature of the polymer electrolyte. Several methods such as blending, plasticization, copolymerization, and addition of ceramic filler additives are in use to modulate the conductivity of the polymer electrolytes. Blending of polymers is a useful and easy method to generate new polymeric materials with enhanced mechanical stability. The conductivity values of PVAc polymer complexes show better when blending with other polymers like PVdF due to its semicrystalline nature. It has been reported that the addition of a plasticizer such as propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) to polymer-salt complexes forms gel-type electrolytes which in turn increase the conductivity [5]. Polymers investigated as gel electrolytes for lithium-ion batteries include poly(ethylene oxide) (PEO), [6, 7] polyacrylonitrile, [8] poly(vinylidene fluoride) (PVdF), [9–12] poly(methyl methacrylate) [13–16], and Poly(vinyl acetate) (PVAc) [17]. The aim of the present work is to find a good plasticizer which provides more ion-polymer interactions in the PVAc/PVdF-$LiClO_4$ gel polymer electrolyte by using conductivity studies, SEM, and FT-IR studies. Lithium perchlorate salt was chosen because of its smaller ionic radius, smaller dissociation energy, and the high solubility in most of the organic solvents [18].

Materials and methods

The gel polymer electrolytes were prepared by the simplest method for electrolyte thin films, the solution-casting technique. PVAc (Mw 140,000), PVdF (Mw 534,000), γ-butyrolactone (GBL, purity >99 %), propylene carbonate (PC, purity 99 %), and lithium perchlorate salt ($LiClO_4$, ≥95 %) were obtained from Sigma-Aldrich, USA. The solvent tetrahydrofuran GR (THF) from Merck, Germany and dimethyl carbonate (DMC, purity 99 %) and diethyl carbonate (DEC, purity 99+%) from Alfa Aesar, India were used as received. The appropriate quantities of polymer and salt [PVdF

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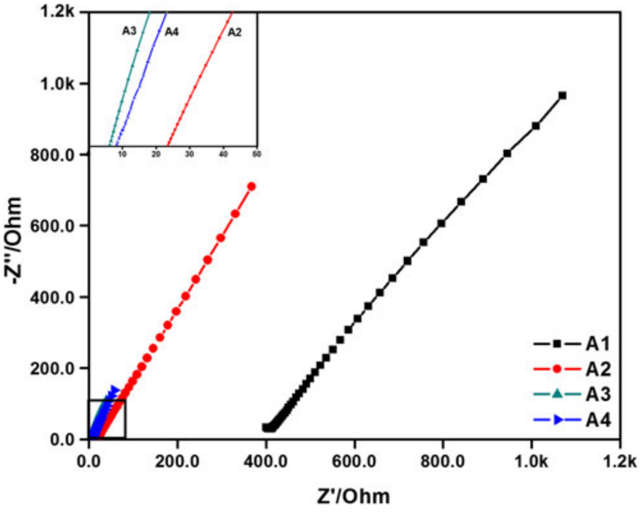


Fig. 1 Typical impedance plots of polymer electrolytes PVAc/PVdF/$LiClO_4$/X [X=DMC(A1), DEC(A2), PC(A3), and GBL(A4)]

(20 wt%) - PVAc (5 wt%) - $LiClO_4$ (8 wt%) - plasticizer (67 wt%)] were dissolved in the solvent tetrahydrofuran separately. The dissolved polymer solution, salt, and plasticizers were mixed together, and the solution was stirred with the help of a magnetic stirrer continuously to obtain a homogeneous mixture. Finally, the polymer solution was allowed to evaporate THF slowly, and the obtained jelly solution was cast on petri dishes. To remove the residual traces of THF, the films were further dried at 60 °C for 12 h. The resulting films exhibited free-standing nature (thickness 0.3–0.5 mm).

Thin films were subjected to Fourier transform infrared (FT-IR) study to investigate the complexation behavior. FT-IR spectroscopic studies were carried out using the JASCO FT-IR 460 (plus) (Japan) spectrometer in the range of 400–4,000 cm^{-1}. The a.c. impedance study was carried out on the polymer electrolyte films with stainless steel blocking electrodes by using a computer controlled μ-AUTOLAB type-III potentiostat/galvanostat in the frequency range of 100 Hz–300 KHz for various temperatures ranging from 303 K–343 K. The activation energy (E_a) values were determined by temperature-dependent conductivity studies. JEOL, JSM-840A scanning electron microscope (SEM) model was used for microstructural studies.

Results and discussion

Conductivity studies

The ionic conductivity of the solid polymer electrolyte (PVAc/PVdF/$LiClO_4$) system was derived from the complex impedance plots. Figure 1 shows that the typical impedance plot for PVAc/PVdF-blended gel polymer electrolytes over the frequency range of 100 Hz–300 kHz at 303 K. The bulk resistance, R_b calculated from the intercepts on the x axis (Z') in the impedance plot.

The ionic conductivity is calculated using the equation:

$$\sigma = t/R_b A \tag{1}$$

where t is the thickness of the polymer electrolyte membrane (thickness 0.03–0.05 cm) and A is the area of membrane-electrode contact (area 3.14 cm^2).

Table 1 shows the dielectric constant and viscosity values of the organic solvents used and the conductivity values of the prepared gel polymer electrolytes which vary from 0.097×10^{-2} S cm^{-1} to 0.922×10^{-2} S cm^{-1} at room temperature. The variation in the conductivity is due to the difference in both the mobility and charge-carrier concentration of electrolytes which is enhanced by the high dielectric constant of the plasticizer used. The similar effect has been reported by Sekhon et. al and Ulaganathan et. al [19, 20] for PVC/PEMA- and PVAc/PVdF-HFP-blended systems, respectively. From the impedance plot, it is observed that when the dielectric constant of plasticizers increases, the bulk resistance values of the blended systems are decreased.

Temperature dependence of ionic conductivity

Figure 2 shows the temperature variations of the conductivity of all the polymer blend complexes. From the plot of log σ versus the inverse of temperature (T), it is understood that PVdF/PVAc/PC/$LiClO_4$ complex film exhibits higher conductivity value of the order of 10^{-2} S cm^{-1} at 303 K. The bulk resistance values are decreasing with the increase in temperature. The ionic conductivity values are found to increase from 0.922×10^{-2} S cm^{-1} to 1.327×10^{-2} S cm^{-1} when the

Table 1 Dielectric constant and viscosity values of plasticizers and the measured conductivity values

Organic solvent	Dielectric constant [24]	Viscosity at 25 °C (cP) [24]	PVAc/PVdF/$LiClO_4$/X	Conductivity σ (S cm^{-1})$\times 10^{-2}$ at 303 K	Activation energy, E_a (eV)
DMC	3.12	0.59	X=DMC	0.215	0.83
DEC	2.82	0.75	X=DEC	0.097	1.03
PC	64.4	2.5	X=PC	0.922	0.42
GBL	39.1	1.7	X=GBL	0.770	0.50

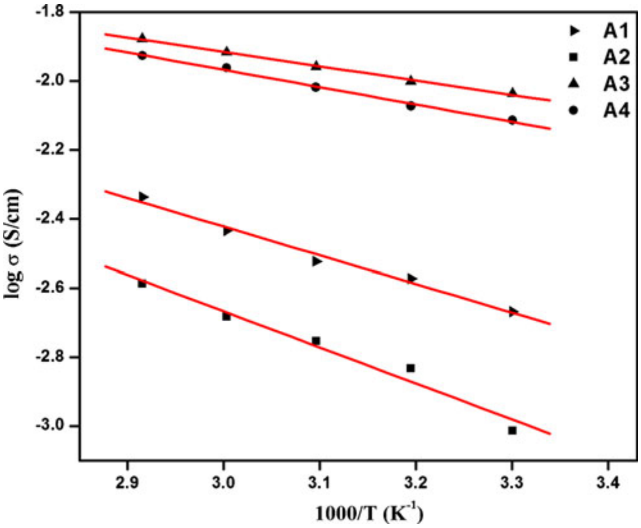


Fig. 2 Temperature dependence of ionic conductivity for PVAc/PVdF/$LiClO_4$/(X) X=DMC(A1), DEC(A2), PC(A3), and GBL(A4)

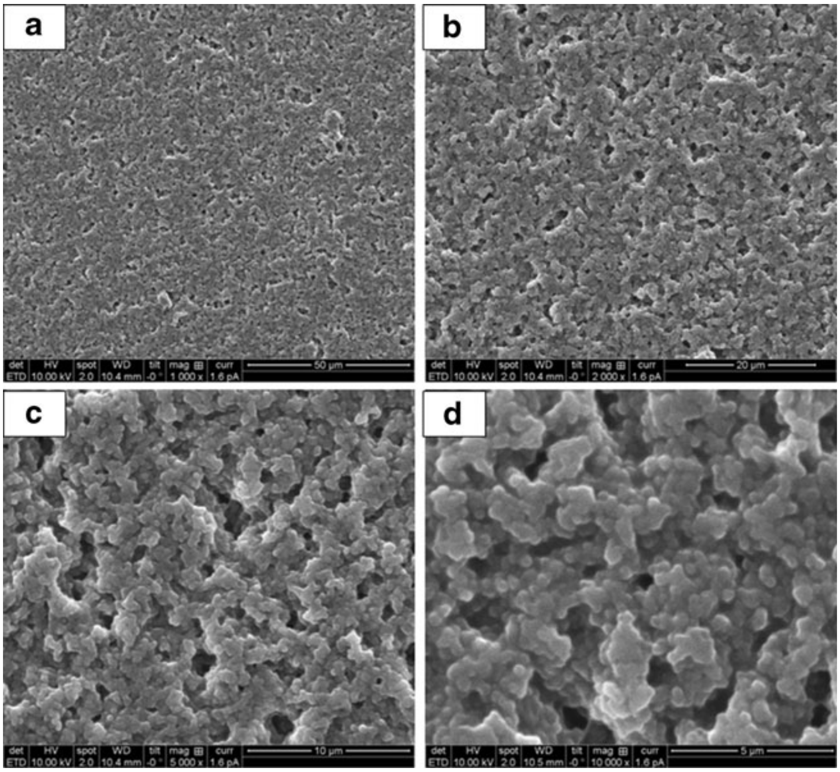
temperature increases from 303 to 333 K, and the films are found to be mechanically stable. At higher temperatures, thermal movement of polymer chain segments and the dissociation of salts improved, which in turn increases the conductivity. It is observed that the increase in temperature leads to an increase in the conductivity value for all the compositions. From the plot, it has been observed that as the temperature increases, the ionic conductivity also increases for all the polymer electrolytes, which can be rationalized by the free-volume model [21]. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules, or polymer segments can move into the free volume easily. The resulting conductivity represented by the overall mobility of ion and polymer is determined by the free volume around the polymer chains. Therefore, as the temperature increases, the conductivity increases. This leads to an increase in ion mobility and segmental mobility that will assist ion transport [22]. The plasticizer PC having high dielectric constant would dissolve enough charge carriers and provide more mobile medium (amorphous region) for the ions so as to enhance the conductivity behavior of the resultant samples [23, 24].

The linearity in temperature dependence of conductivity plot indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion. The linear behavior of the plots suggests that the data can be better described by the Arrhenius type equation:

$$\sigma = \sigma_o exp(-E_a/kT)\left[\mathrm{Scm}^{-1}\right] \tag{2}$$

where σ_o is the preexponential factor, k is the Boltzmann constant, and E_a is the activation energy (in eV). The E_a values, for all the compositions, were computed from linear fitting of the above equation and listed in Table 1. The solid polymer electrolyte containing PC shows low activation energy E_a ~0.42 eV, may be due to the increase in the degree of amorphicity as compared to the other polymer-salt compositions, and it is indicative of a relatively easier ion migration in

Fig. 3 SEM image of PVAc/PVdF/$LiClO_4$/PC (A3) gel polymer electrolyte at different magnifications



the system. The activation energies are found to be significantly larger than 0.15 eV (14.5 kJ/mol) typical for Li-salt solutions with organic solvents. This indicates strong interaction between the polymer matrix and the electrolyte ions within the system. For application in devices operating over a wide range of temperature, it is desirable to have electrolytes with uniform conductivity. Therefore, electrolyte systems with low activation energies are desirable.

SEM analysis

Scanning electron microscopic (SEM) images of porous polymer film having high conductivity with different magnifications are shown in Fig. 3. The image shows uniformly distributed spherical structures in the electrolyte system, and the average size of these spherical structures appears to be the same. It is found that the pores of 0.5–2 μm on the surface of the polymer matrix are developed by the evaporation of solvent during casting technique. Rhoo et. al [25] reported that the formation of the porous structure is a complex process that depends on the interaction of the solvent with the polymers and the relative rates of the evaporation of compounds. The presence of a plasticizer-rich phase shows a homogeneous pore structure, which leads to ion mobility, hence higher conductivity. It is noted that there is no apparent interface between the two polymers, which indicates that PVdF and PVAc have good compatibility with the plasticizer.

FT-IR analysis

FT-IR spectroscopy has been used to analyze the interactions among the atom or ions in the electrolyte system. These interactions can induce changes in the vibrational modes of the molecules in the polymer electrolyte.

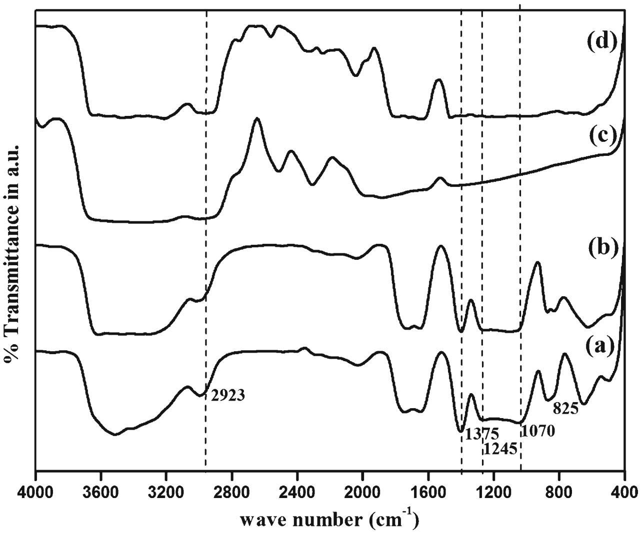


Fig. 4 FT-IR spectra of the prepared samples such as PVdF/PVAc/LiClO$_4$/X [X=DMC (**a**), DEC (**b**), PC (**c**), and GBL (**d**)]

The vibrational bands at 2,923, 2,865, and 1,375 cm^{-1} could be ascribed to –CH$_3$ asymmetric stretching, symmetric stretching, and symmetric bending vibrations respectively [26]. Also, the vibrational band at 1,245 cm^{-1} is assigned to C–O–C symmetric stretching vibration of pure PVAc. In pure PVdF, the stretching frequencies of C–F and CF$_2$ show vibrational bands at 1,263 and 1,186 cm^{-1}. Also, the symmetric C–C stretching and CF$_2$ bending vibrations of pure PVdF, respectively, show vibrational peaks at 1,070 and 533 cm^{-1}. The bending and symmetric stretching vibrations of perchlorate (ClO$_4^-$) anion in the LiClO$_4$ give vibrational peaks at 1,070–1,060 and 940–925 cm^{-1} [27]. Table 2 shows the vibrational assignments of pure PVdF and PVAc.

The FT-IR spectra of PVAc/PVdF/LiClO$_4$ complexes with various plasticizers are shown in Fig. 4. From Fig. 4a, d, it has

Table 2 Vibrational peaks of pure samples

Peaks (cm^{-1})	Attribution	Sample	References
2,923	CH$_3$ asymmetric stretching	Pure PVAc	[22]
2,865	CH$_3$ symmetric stretching	Pure PVAc	[22]
1,375	CH$_3$ bending vibration	Pure PVAc	[22]
1,245	C–O–C symmetrical stretching	Pure PVAc	[22]
1,100	C–O stretching vibration	Pure PVAc	[22]
1,090	C–C stretching vibration	Pure PVAc	[22]
1,730	C=O stretching	Pure PVAc	[22]
940	per chlorate symmetric stretching	Pure LiClO$_4$	[23]
1,382	C–F stretching vibration	Pure PVdF	[23]
1,263	C–F stretching frequency	Pure PVdF	[23]
533	CF$_2$ bending vibration	Pure PVdF	[23]
1,224	CF$_2$ stretching vibration	Pure PVdF	[23]
1,186	CF$_2$ stretching frequency	Pure PVdF	[23]
1,070	C–C symmetric stretching	Pure PVdF	[23]

been observed that the stretching frequency at 1,734 cm^{-1}, which corresponds to C=O of pure PVAc, is shifted to 1,746–1,721 cm^{-1}. The shift observed in the carbonyl stretching frequency of complexes when compared to pure PVAc indicates the formation of complex. The absorption peaks corresponding to DMC (795, 920, 990, and 1,520 cm^{-1}), DEC (2,991, 1,639, 1,379, and 1,272 cm^{-1}), PC (1,340 and 849 cm^{-1}), and GBL (1,648, 1,280, and 676 cm^{-1}) [28] are found to be shifted in their respective complexes. This shift in vibrational peaks confirms that the strong interaction takes place between the plasticizer and the polymer-salt system. The broad absorption region 3,250–3,750 cm^{-1} present in all the complexes may be due to the symmetric stretching of –OH in the carbonyl group or the moisture absorption while the sample is loaded for analysis. The shift observed in the ClO_4^- anion at 925 cm^{-1} in the blend polymer complexes has been used as an indicator for the dissociation of $LiClO_4$ [29]. In addition to the above mentioned absorption peaks, some new peaks are also observed in the complexes. All these observations in the FT-IR spectra clearly indicate that both polymers PVdF and PVAc are complexed with salt and plasticizer.

Conclusions

PVdF/PVAc/$LiClO_4$ blend gel polymer electrolytes with different plasticizers have been prepared by solution-casting technique. The existence of the complex has been confirmed by the presence of new shoulder peaks and broadening and shifting of bands in the FT-IR spectra. Ionic conductivity of the polymer electrolytes has been measured in the temperature range of 303–343 K. All electrolytes show good ionic conductivity at room temperature. The blend polymer electrolytes containing propylene carbonate (PC) exhibits the highest conductivity 0.922×10^{-2} S cm^{-1} at room temperature because of the higher dielectric constant as compared to other plasticizers used in the present study. This reveals that the blend polymer electrolyte can be a good candidate for Li rechargeable battery. Increase in ionic conductivity can be attributed to the fact that high dielectric constant of plasticizer enhances the porous structure and amorphous nature of the gel polymer electrolytes forming better connectivity for ion motion. This is confirmed by SEM results.

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