Preparation and characterization of plasticized high molecular weight PVC-based polymer electrolytes

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Abstract. Poly(vinyl chloride) (PVC)-based polymer electrolytes films consisting of lithium trifluoromethanesulfonate (LiCF_3SO_3)-ethylene carbonate (EC) were prepared by the solution-casting method. Ionic conductivities of the electrolytes have been determined by an impedance studies in the temperature range of 298–373 K. Complexation of the prepared electrolytes is studied by X-ray diffraction (XRD) analysis. Thermogravimetric analysis (TGA) was used to confirm the thermal stability of the polymer electrolytes. The conductivity–temperature plots were found to follow an Arrhenius nature. All these films are found to be thermally stable until 132–167°C.

Keywords. High molecular weight poly(vinyl chloride); plasticizer; polymer electrolyte.

1. Introduction

In the recent years, polymer electrolytes have been widely studied due to their applicability for a variety of solid state and electrochemical device application including batteries, fuel cells, supercapacitors, electrochromic devices and chemical sensors (Santhosh *et al* 2006). Polymer electrolytes have many advantages, such as flexibility, ease of processing into thin films of large surface area, electrochemical stability and leak-proof nature (Bhide & Hariharan 2006). In the past two decades, different polymer host, such as poly(ethylene oxide) (PEO), poly(methylmethacrylate) (PMMA), poly(acrylonitrile) (PAN) and poly(vinyl chloride) (PVC) have been studied (Stephen 2006).

The widespread use of PVC is attributed mainly to the presence of lone pair electrons at the chlorine atom where inorganic salts can be solvated and the dipole–dipole interaction between the hydrogen and chlorine atoms can stiffen the polymer backbone (Uma *et al* 2005).

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PVC allows the formation of homogeneous mixture films when blended with Li salt and EC plasticizer; but these gel systems are essentially thermodynamically unstable and may undergo solvent exudation upon long term storage, especially under open-atmosphere conditions. This phenomenon is known as the 'syneresis effect'. When this effect occurs, the solvent will leak to the surface of the electrolyte film and induces the film to become turbid (Li *et al* 2006).

Plasticized polymer electrolytes have proved to be promising as electrolytes of the lithium batteries owing to their high ionic conductivity (Sun *et al* 2004). The enhancement in electrical conductivity in plasticized electrolytes is explained in terms of ion association/dissociation effect and increase in the amorphous nature of the system (Pradhan *et al* 2005). However, such plasticized electrolytes also exhibit drawbacks, such as reactivity of polar solvents with lithium electrode, poor mechanical properties at high degree of plasticization and solvent volatility (Cha *et al* 2004).

In the present work, high molecular weight PVC-based film consisting of LiCF_3SO_3 and ethylene carbonate (EC) was characterized by impedance spectroscopy, XRD and TGA analysis. This is to study the conductivity, crystallinity behaviour and thermal stability of the films.

2. Experimental procedure

2.1 Sample preparation

The preparation of polymer electrolytes was carried out by solution cast technique with tetrahydrofuran (THF) as solvent. The appropriate amount of high molecular weight PVC, LiCF_3SO_3 and different ratios of EC were mixed and stirred for 24 hours to achieve a homogeneous, viscous solution. The solution thus obtained was cast on a glass plate and allowed to evaporate slowly inside a dessicator.

2.2 Ionic conductivity measurements

Conductivity measurement was performed by impedance spectroscopy using HIOKI Model 3532-50 bridge interfaced to a computer for data acquisition over frequency range of 50 Hz to 1 MHz. The films were sandwiched between two stainless disk electrodes. The conductivity temperature study was conducted in the temperature range of 25°C to 100°C.

2.3 XRD analysis

X-ray diffraction analysis was performed using Control Software MXP3 model from Japan MAC SCIENCE in the 2θ range between 5° and 45° with scanning rate at 5°/min.

2.4 TGA analysis

Thermal stability of the electrolytes was studied using METTLER 851° TGA. The samples were put in an Al pan and heated from 25°C up to 350°C at the rate of 10°C/min.

3. Results and discussion

3.1 Ionic conductivity

The ionic conductivity is calculated using the equation $\sigma = l/(R_B A)$, where l is the thickness of the polymer electrolyte film, A is the surface area of the film and R_B is the bulk electrical

Figure 1. Impedance spectrum of PVC-LiCF₃SO₃: EC (60:40) at curve (a) 25°C, (b) 50°C and (c) 70°C.

resistance value, which can be calculated from the intercept on the Z' axis (Fan & Maier 2006). The ionic conductivity of the polymer electrolyte depends on the effective number of carrier ions and the ions mobility. The effective number of carrier ions is related to the concentration of the dissolved ions. The ion mobility in a polymer electrolyte formed by the dissolution of ions in the polymer is facilitated by the segment mobility of the polymer chains (Santhosh *et al* 2006). Figure 1 shows the relationship between temperature against ionic conductivity of PVC-LiCF₃SO₃: EC (60:40) system. As the temperature increases, the R_B value will decrease and show a higher conductivity value according to the equation above. The conductivity at room temperature is $2.29 \times 10^{-8} \text{ S cm}^{-1}$, it then rises to $2.56 \times 10^{-8} \text{ S cm}^{-1}$ and subsequently $2.77 \times 10^{-8} \text{ S cm}^{-1}$ as the temperature increases from room temperature to 50°C and 70°C respectively. This is due to the segmentation of the polymer network as well as an increase in the amorphous nature.

Figure 2 shows the relationship between $\log \sigma$ against $1000/T$ for PVC-LiCF₃SO₃: EC (75:25) and PVC-LiCF₃SO₃: EC (60:40). The regression value R^2 lies in 0.9710 and 0.9954 for 25 and 40 wt.% EC respectively. These values are close to unity and therefore the temperature-dependent ionic conductivity for all the complexes obey Arrhenius rule, indicating that the conductivity mechanism is thermally assisted (Yahya & Arof 2003). Since the conductivity temperature data follows Arrhenius behaviour, the nature of cation transport is quite similar to that in ionic crystals, where ions jump into neighbouring vacant sites (Ramesh *et al* 2002).

Figure 3 shows that the ionic conductivity increases with the increase of plasticizer content at room temperature. The maximum conductivity value of $4.02 \times 10^{-8} \text{ S cm}^{-1}$ is obtained at 35 wt.% of the plasticizer content and decreases again at EC content of 40 wt.%. This decrease in conductivity could be due to ion aggregation. This is because ion aggregation decreases the available number of charge carriers. It can be concluded that CF₃SO₃⁻ increases the dissociation of the LiCF₃SO₃ salt into lithium and triflate ions up to a certain concentration

Figure 2. Temperature dependence of ionic conductivity of (a) PVC-LiCF₃SO₃: EC (75:25) and (b) PVC-LiCF₃SO₃: EC (60:40).

after which ion aggregation occurs at a faster rate than ion dissociation by CF₃SO₃⁻ and reduces the number of mobile ions in the sample.

Ionic conductivity of the enhanced plasticized solid polymer electrolyte can be explained by the interaction between PVC, EC and LiCF₃SO₃. There are three main interactions among

Figure 3. Variation of conductivity with plasticizer (EC) weight percentage at 25°C.

them: (i) ion–ion interaction between Li^+ cations and CF_3SO_3^- anions; (ii) ion–dipole interactions between Li^+ cations and chlorine in PVC; (iii) ion–molecule interactions between Li^+ and EC. These interactions are of importance to form PVC- LiCF_3SO_3 -EC polymer electrolyte, in which three different compounds of PVC- Li^+ , PVC- Li^+ -EC and Li^+ -EC exist. The oxygen of $\text{C}=\text{O}$ in EC is an electron donor which will participate in competition with CF_3SO_3^- and PVC. The Li^+ -EC interactions exist not only between Li^+ and oxygen atoms of $\text{C}=\text{O}$ group, but also between Li^+ and another two oxygen atoms in the ring structure of EC. Li^+ -EC interaction plays an important role in the conductivity of PVC- LiCF_3SO_3 -EC system. The addition of EC leads to the formation of Li^+ -EC complex and enhances the flexibility of PVC chains by decreasing the fraction of PVC- Li^+ complex. The increase in flexibility is the reason why the conductivity increases with the addition of EC plasticizer (Qian *et al* 2002).

3.2 XRD analysis

The X-ray diffraction analysis is used to determine the structure, complexation and crystallization of the polymer matrix (Vickraman & Ramamurthy 2006; Pradhan *et al* 2005; Rajendran *et al* 2004). In order to investigate the effect of complexation of PVC- LiCF_3SO_3 -EC system, XRD analysis has been performed and the respective diffraction patterns of pure high molecular weight PVC, PVC- LiCF_3SO_3 and PVC- LiCF_3SO_3 -EC are shown in figure 4.

For pure PVC curve, two broad amorphous peaks are formed and shown at $2\theta = 9.36^\circ$ and 17.40° . When Li salt was added, the peaks shifted to 9.94° and 18.36° , respectively. Upon addition of plasticizer, the peaks shifted to 9.76° and 18.50° . The characteristic diffraction lines for the lithium salt are absent in the PVC- LiCF_3SO_3 and PVC- LiCF_3SO_3 -EC complexes. This is observed from the intensity of the peaks which are same for all the three samples studied. This shows that the amorphous nature of the pure polymer is retained with the addition of salt and plasticizer. This behaviour demonstrates that complexation between PVC, LiCF_3SO_3 and EC occurs and takes place in the amorphous region (Rajendran *et al* 2004).

Figure 4. XRD patterns of (a) pure PVC, (b) PVC- LiCF_3SO_3 and (c) PVC- LiCF_3SO_3 -EC.

Figure 5. TGA analysis of pure PVC and PVC-LiCF₃SO₃.

3.3 TGA analysis

TGA has been used to investigate the thermal degradation, phase transition and crystallization of the polymers. For lithium ion battery, it is necessary for the polymer electrolyte to have high thermal stability. In order to ascertain the thermal stability, the prepared films were subjected to TGA analysis (Stephen *et al* 2002).

The thermogravimetric curve for pure PVC and PVC-LiCF₃SO₃ films are given in figure 5. The pure PVC film appears to be quite dry since its weight is almost constant up to 100°C. Above 100°C, i.e. after complete dehydration, no further weight loss is observed until irreversible decomposition commenced at approximately 138°C and shows a weight loss of 8.51%. This indicates that the film is stable up to 138°C. The loss may be due to decomposition of PVC occurred (Stephen *et al* 2005). When the temperature rose to 293°C, the samples exhibit a gradual weight loss of about 60%. This shows that the occurrence of another irreversible decomposition took place half of the PVC weight vanished.

For the PVC-LiCF₃SO₃ film, a weight loss about 9% at 100°C is observed. This is due to the removal of moisture or residue solvent in the film (Uma *et al* 2004). The first decomposition took place at 171°C which induced 7% weight loss and second decomposition occurred at 304°C which showed weight loss of 35%. Obviously, this indicates that the film is stable up to 171°C and demonstrates that PVC-LiCF₃SO₃ is preferred in the lithium polymer batteries as its operating temperature is normally in the range of 40°C–70°C (Uma *et al* 2005).

Figure 6. TGA analysis of PVC-LiCF₃SO₃: EC (90:10), PVC-LiCF₃SO₃: EC (75:25) and PVC-LiCF₃SO₃: EC (60:40).

Since the first decomposition of PVC-LiCF₃SO₃ film occurred at higher temperature and bore a lower weight loss, this proves that the thermal stability increased with addition of LiCF₃SO₃.

The TG curve which contains 10, 25 and 40 wt.% of EC in PVC-LiCF₃SO₃ films are illustrated in figure 6. At temperature around 100°C, a small amount of weight loss is observed for these three samples. This is considered as the result of loss of solvent and moisture from the electrolytes as mentioned before. The first decomposition occurred at temperature 167°C, 160°C, 132°C respectively which suffered weight loss from 12% to 22 and 23% as the plasticizer content increase. This shows that the thermal stability decreased with increase in plasticizer content. Subsequently, the second decomposition showed a weight loss of 25–37% at the temperature range of 291–308°C for all three samples.

Polymers of higher PVC content and lower plasticizer amount are proven to have a relatively good stability as they have the first decomposition at higher temperature bearing a lower weight loss. Also, the sample with 10 wt% EC shows the lowest ionic conductivity followed by the samples with 25 and 40 wt% EC. Figure 2 shows that the conductivity of 25 wt% EC is lower than 40 wt% EC at all temperatures. This is due to high thermal stability of the polymer

films which will restrict the movement of ions. Hence, it results in minimum conductivity for the high thermal stability polymer films.

4. Conclusion

The impedance study showed that the addition of plasticizer to the polymer electrolyte enhanced the ionic conductivity. The temperature-dependent ionic conductivity plots of the electrolyte films seem to obey Arrhenius rule. XRD analysis confirms the complexation occurred between EC, PVC and LiCF_3SO_3 . TGA study showed that addition of plasticizer caused a lower thermal stability.

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