

IONIC CONDUCTANCE STUDIES ON POLY (VINYL CHLORIDE) - ZnO AND PVC-ZrO₂ POLY ELECTROLYTE SYSTEMS

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Abstract: Conductance study of various conducting polymer electrolyte systems consisting of Poly (vinyl chloride) as the host polymer, with lithium per chlorate (LiClO₄), ZnO and ZrO₂ as added salts is presented here. The solid polymer electrolytes were prepared by employing solution casting method. The ionic conductivity of polymer electrolyte systems has been investigated by using impedance spectroscopy technique at a wide range of temperature. Various systems showed different conductance behavior. Among the two added salts i.e. ZnO and ZrO₂ electrolyte system of ZrO₂ showed highest conductivity values at room temperature. The addition of single plasticizer enhanced the conductance in this system. The conductance trend in these systems at room temperature was as: PVC – ZrO₂-EC-LiClO₄, PVC – ZnO – LiClO₄.

Key Words: Ionic conductivity, polymer electrolyte, plasticizer, PVC, inorganic filler, impedance studies.

Introduction

The main objective of the polymer research is focused on the development of polymer electrolyte which exhibits high ionic conductivity in addition to high mechanical strength. These materials are much lighter and can easily be processed. Polymer electrolytes with high ionic conductivity, sufficient mechanical strength and thermal strength are extensively investigated because of their application in solid state batteries, sensors, fuel cells and electrochemical windows, etc., (Subban and Arof, 2004; Anantha *et al.*, 2005), cellular telephones, and smart credit cards (Osman *et al.*, 2001; Choi *et al.*, 1998). These polymer electrolytes have drawback of low conductivity.

Composite polymer electrolytes containing polymer-salt complex with second

phase are also being investigated. The presence of finely dispersed inorganic particles in the polymer matrix has proven to be very useful in the improvement of membrane performance. The addition of dispersed second phase particle is generally believed to enhance the conductivity values (Baskaran *et al.*, 2007; Zygadlo-Monikowski *et al.*, 2007; Krawiec *et al.*, 1995; Ogata *et al.*, 1995). A variety of possible combinations of organic/inorganic composite material make it useful for improving the thermal properties of inorganic content with flexibility and ductibility of organic polymer portion. Poly (ethylene oxide) based polymer electrolytes have been extensively studied (Alloin *et al.*, 1997; Rajendren and Uma, 2000). The reports on other polymer hosts are very few (Mohamad and Arof, 2007; Periasamy *et al.*, 1999).

Poly(vinyl chloride) PVC based electrolytes are widely prepared because they are inexpensive, easily processable, have good mechanical strength and are compatible with most solvents or plasticizers (Tambelli *et al.*, 2002). PVC can act as mechanical stiffener in the electrolyte due to lone pair of electrons at the chlorine atom where inorganic salt can be solvated. Furthermore, the dipole-dipole interaction between the hydrogen atom and chlorine atom can also stiffen the polymer backbone (Zaheruddin, *et al.*, 1992). An amorphous polymer structure is preferred for good conductivity. As PVC is low crystalline (Cho and Sekhon, 2006) so, its composites are studied with great interest.

As mentioned earlier, pure polymer electrolytes have potential to be used in various applications but their low conductivity restricts their use. The low conductivity of these polymer electrolytes is attributed to their semi crystalline nature. The suppression of the crystallinity and creation of a stable amorphous phase imparts conductivity. The incorporation of suitable amount of plasticizer brought the advancement in increasing the ionic conductivity of these polymer electrolytes. Generally, low molecular weight, high dielectric constant polar organic solvents such as ethylene carbonate, propylene carbonate, polyethylene glycol, etc. are used as plasticizers. Various studies on plasticized PVC electrolytes (Seeripathy *et al.*, 1994; Andrieu *et al.*, 1995; Agnihotry and Gupta, 1996) are given in literature.

The effects of various fillers in PVC-based electrolytes are not fully investigated. In this paper, a systematic study on composite polymer electrolytes of PVC, LiClO_4 , ZnO and ZrO_2 with ethylene carbonate is reported

in order to look for good lithium ion conducting polymer electrolyte.

Materials and Methods

Materials

Poly (vinyl chloride) (PVC, average mol. wt. 1.5×10^5) from Aldrich, USA was used in the present study. It was dried at 100°C for 12h before further processing. The plasticizers like ethylene carbonate (EC), and propylene carbonate (PC) (E. Merck, Germany) were used as such without any further purification. The lithium salt LiClO_4 (Aldrich, USA) was kept under vacuum at 70°C for 24 h before use. Special grade tetrahydrofuran (THF, E. Merck, and Germany) was used as received. The inorganic fillers i.e. ZnO & ZrO_2 were used without any further purification.

Preparation of Solid Polymer Electrolyte Systems

Poly (vinyl chloride) solution (5%) was prepared in tetrahydrofuran solvent and stirred by using a magnetic stirrer to obtain a homogenous solution. 1 g of LiClO_4 and appropriate amount of filler was then added in to this solution. The resulting mixture was stirred for about 48 h and then poured in to a petridish. Thin electrolyte films were obtained by slow drying at room temperature. The THF was completely evaporated to obtain dried films. The resulting thin films were then peeled off from petri dish. These steps were repeated for preparation of all PVC electrolytes. The thin films of various concentrations were kept in a desiccator. The films were further dried in vacuum oven before impedance analysis. All the polyelectrolyte systems were prepared in this

way. These systems are: PVC-ZrO₂-EC-LiClO₄ and PVC-ZnO- LiClO₄.

Sample Characterization

The prepared samples of solid polymer electrolyte systems were subjected to AC impedance measurements by Hioki 3522-50 LCR Hi tester, Japan at various temperatures. The measurement of ionic conductivity was carried out by sandwiching the solid polymer electrolyte films between two polished stainless steel disk electrodes of diameter 8mm which acted as blocking electrode for ions. The electrodes with sample were sealed in an air tight container. The polymer electrolyte samples were cut into pieces with diameter of about 15 mm. The study was carried out in the frequency range of 1 mHz - 100 KHz. From Nyquist plots, the bulk resistance was determined and then the conductance was calculated as a normal procedure. The temperature dependent conductivity of these samples was performed at 5 °C intervals in the temperature range of 20-90 °C. For this purpose, the sandwiched film assembly was hung in air tight glass jar having thermometer near the film. This jar was immersed in water bath with controlled temperature. The temperature was adjusted to the required value and checked with a thermometer near sample film.

Results and Discussion

PVC composite with LiClO₄ using one plasticizer i.e. EC was studied as reference starting material while the ZnO and ZrO₂ were then studied in order to see the effect of their addition to polymer electrolyte conductance. Fig.1 shows the influence of temperature on the ionic conductivity of PVC-EC- LiClO₄ polymer electrolyte system.

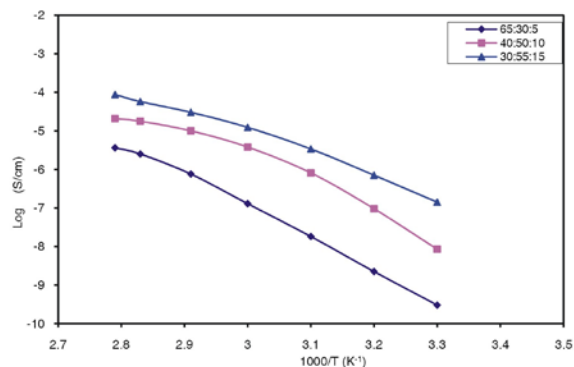


Fig. 1. Temperature dependence of ionic conductivity for polymer electrolyte system of PVC:EC:LiClO₄.

Various combinations of the three components are given. The ionic conductivity of the polymer electrolyte films increased considerably with increase in temperature as it is usually shown in literature (Wang and Qian, 1996). Figure also depicts the effect of concentration of salt on the ionic conductivity of the films which showed that with the increase in concentration of salt, ionic conductivity also increases (Floriańczyk *et al.*, 1991) which may be due to increase in the number of mobile ions in the solid polymer electrolytes. The highest conductivity of $1.41 \times 10^{-7} \text{ Scm}^{-1}$ was shown by 30:55:15 composite of PVC: EC: LiClO₄. It was also found that ionic conductivity exhibited inverse relation with the PVC content in the polyelectrolyte systems. Increase in PVC content decreases the conductivity of the system (Bischoff *et al.*, 1993).

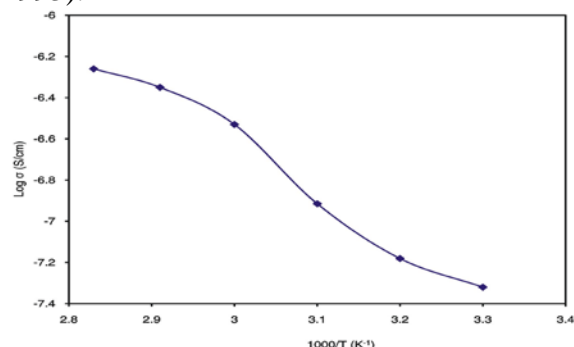


Fig. 2. Arrhenius plot for conductivity of PVC-ZnO-LiClO₄ with 25 wt% ZnO.

Fig. 2 shows plot for PVC-ZnO-LiClO₄. It can be inferred from the plot that Arrhenius rule is not followed by PVC-ZnO-LiClO₄ complexed polymer electrolyte systems and a non linear relationship is exhibited by the electrolyte (Chen-Yang and others, 2003). Figure shows that initially at low temperature with the increase in temperature, ionic conductivity increases rapidly while at higher temperature conductivity increase is not fast (Zhou, *et al.*, 2008). If we see overall temperature effect, it is typical i.e., conductance increases with the increase in temperature. The effect of temperature on ionic conductivity at low temperature may be explained on the basis of cohesive energy of polymer chains. When temperature of polymer electrolyte system is increased, the cohesive energy of polymer chains decreases due to decrease in interaction involved between ionic species and polymeric chains thereby improved ionic conductivity of polymer electrolyte system (Santhosh *et al.*, 2006; Bac *et al.*, 2006). This behavior is due to the reason that with the increase in temperature, softening point of polymer electrolytes reduces while segmental motion of polymer chains increases thereby ionic conductivity also increases. But increase in ionic conductivity continues to an optimum concentration beyond which it shows less increase. The variation of ionic conductivity with temperature may also be associated with viscosity of the system and dissociation of salt because when temperature increases then viscosity shows a decrease due to which segmental motion of polymer chains increases thereby showing improved ionic motion (Kuil *et al.*, 2007). While with decrease in temperature viscosity shows increase due to which segmental motion of polymer chains are restricted so, ionic motion decreases. Similarly, with the increase in

temperature, salts can easily be dissociated into its corresponding ions; therefore, ionic mobility increases, while at lower temperatures, salts cannot be dissociated easily into corresponding ions causing a decrease in ionic conductivity.

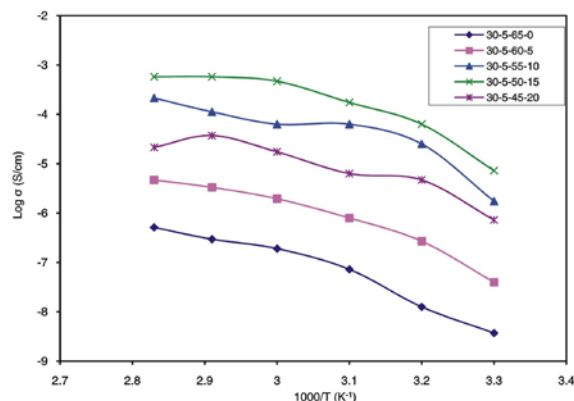


Fig. 3. Arrhenius plot of log conductivity against reciprocal temperature for PVC-LiClO₄-EC-ZrO₂ polymer complexes.

Fig. 3 presents the effect of temperature on ionic conductivity for polymer electrolytes of ZrO₂ added system. It can be found that overall features of the Arrhenius plot are similar for the polymer electrolytes of various compositions containing different content of ZrO₂ (Baskaran *et al.*, 2006). No linear relationship was observed for all samples of polymer electrolyte containing ZrO₂. Nonlinear relationship reveals that the ionic conduction is based on Williams-Landel-Ferry mechanism thereby the results may be effectively explained by Vogel-Tammann-Fulcher (VTF) equation (Aravindan and Vickraman, 2007). Fig.3 also shows the effect of temperature on ionic conductivity of polymer electrolyte containing different concentration of ZrO₂. It can be found that initially there is normal behavior with temperature (Le Nest *et al.*, 1992). This behavior is due to the reason that with the increase in temperature, softening point of polymer electrolytes reduces while segmental

motion of polymer chains increases thereby ionic conductivity also increases. But increase in ionic conductivity continues to an optimum concentration of ZrO₂ beyond which it starts decreasing. The reason is that at high concentration of ZrO₂, crystallite region exists which causes decrease in ionic conductivity. The overall conductance values obtained for different PVC based electrolyte at 30° C are given in Table 1. The decreasing order of conductance is as follows:

PVC- ZrO₂-EC-LiClO₄>PVC-EC-LiClO₄
(30:55:15) > PVC-ZnO-LiClO₄.

Table 1. Conductance values of different PVC based electrolyte at 30 °C

System	Conductance, S cm ⁻¹
PVC-EC-LiClO ₄ (30:55:15)	1.41x10 ⁻⁷
PVC-ZnO- LiClO ₄ (25% ZnO)	4.79x10 ⁻⁸
PVC-ZrO ₂ -EC-LiClO ₄ (18% ZrO ₂)	7.24x10 ⁻⁶

Conclusion

The conductance studies on different PVC based electrolyte systems were undertaken in wide composition and temperature range. Various fillers were added to PVC and thin films were fabricated by solvent cast method. The addition of plasticizer enhances the conductance. Among fillers which we have tried like ZnO and ZrO₂, the conductance values for ZrO₂ are higher than ZnO. The temperature effect is typical for all the systems studied i.e., the conductance increases with increase in temperature.

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